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POWDER METALLOGRAPHY

M. Yu. Bal'shin

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ANNOTATION

This book is an exposition of the theoretical foundations of powder metallurgy - the processes taking place during the deformation and the heat-treatment of metal powders and the accompanying changes in the contact surfaces, structure, and mechanical properties.

The book is designated for use by engineers in the field of metallurgy and metal working, by metallographers, specialists in metaloceramic fabrication, scientific assistants, and also undergraduates of higher technical schools in metallurgy.

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FOREWORD

Until recently metalloceramics, as a branch of science, was not differentiated into powder metallurgy (the manufacturing of products), the metallurgy of powders (manufacturing of powders), and powder metallography (the theory of powder metallurgy).

At the present time, due to the publication of a great number of scientific works on powder metallurgy, the construction of a separate monograph, devoted to the scientific fundamentals of powder metallurgy and powder metallography, became possible.

A very sizable contribution to the creation of the theoretical foundations of powder metallurgy was made by Soviet scientists. The corresponding member of the Academy of Sciences, USSR, Ya. I. Frenkel' laid out the fundamentals of the theory of baking. Academician P. I. Lukirskiy discovered the exceptionally important metallographic phenomena taking place in the baking of rock salt. Honorable mention is merited by the works of engineer V. S. Rakovskiy, a pioneer in the field of scientific literature on metalloceramics in the USSR. The first scientific thesis on powder metallurgy was published by a compatriot of ours, P. G. Sobolevskiy, 120 years ago, in 1827.

Among the foreign scientists, who took a considerable part in the development of the scientific foundations of metalloceramics, it is necessary to mention the author of the well known monograph on powder metallurgy, Dr. V. D. Jones, also professor V. G. Wolfe, and professor F. Zauerwald.

All domestic and foreign sources, published up to January 1947, were utilized in the composition of this book.

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CHAPTER I

INTRODUCTION1. Powder Metallography, Its Place Among Other Branches of Science,
and Its Assignments

Matter is usually classified by its state into solid, liquid, and gaseous, crystalline and amorphous, metallic and non-metallic. Matter may also be classified by the degree of its dispersion and its coherence.

By degree of dispersion, powders and free-flowing bodies, consisting of particles from 0.1 of a micron to several millimeters in size, occupy an intermediate position between compact bodies with particle sizes greater than several millimeters, and colloidal bodies with particle sizes from 0.001 to 0.1 of a micron.

The degree of dispersion alone is inadequate for the characterization of these groups of bodies - they are also differentiated by the degree of coherence of their structural elements. For instance, compact metals consist of dispersed grains of the same magnitude as the particles of metal powders, but the degree of coherence between these dispersions is different. By degree of coherence, powder and free-flowing bodies also occupy an intermediate position between colloidal and compact bodies.

The colloid particles in colloidal solutions are isolated from each other. By contrast, the particles of powders are always in contact with each other, directly or through a thin interlayer of surface admixtures. The particles of free-flowing

bodies, by the nature of their contacts, are also differentiated from the grains of compact metals. The surface of actual contact of the particles in non-compressed powders occupies an insignificant fraction (usually less than 0.001 of a percent) of the entire surface of the particles. The contact between the grains in compact metals is effected practically along their entire surface. The magnitude of the contact surface between the particles of a powder, as will be seen further below, is in direct ratio to the applied pressure, while the area of contact between the grains of a compact metal is almost independent of pressure.

In each (or practically in each) section of the contact surface between the powder grains, rather considerable stresses are localized, while in non-cold-hardened compact metal, the inter-granular contact areas are free from stresses. In compact bodies, porosity is insignificant, while in powders it constitutes a considerable part of their volume. Coherence between the grains of compact metals is strong, and when fractures occur, they take place not along the surface of the crystallites, but inside the latter. The coherence between the particles of powders is weak, and the separation of particles from each other occurs almost exclusively along their surface. This weak coherence is due to the low magnitude of the contact surface, the presence of surface admixture films, and the localization of considerable stresses in the contact areas. In the case of compact metals, the deformation of each individual grain reproduces almost with precision the changes in the form of the adjacent crystallites, as well as the en-

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tire grain conglomerate. For instance, in compressing a compact metallic body to half its size, the corresponding cross-section of the grains is also decreased by half. In the deformation of free-flowing bodies, the particles are deformed not throughout their volume and not throughout their surface, but predominantly in small sections directly adjacent to the surface of mutual contact. Therefore, the particles of powders are, to a considerable degree, individually separated, and their deformation occurs to some degree more or less independently of other particles in direct contact with them. The deformation of the particles is not an exact reproduction of the deformation of the entire free-flowing material, which, to a considerable degree is due to the change in the size of the pores. Thus, it may happen that in the compressing of a free-flowing material to a part of its original volume, the corresponding cross-section of its particles may not change at all.

Metal powders (and to some extent the powder metals derived from them) may be relegated to the large group of bodies with incomplete (partial) contacts between their structural elements. (The term "metal powders", as used in this book, embraces also free-flowing metallic materials with large particles (for instance, chips, shavings, and the like)).

The term "powder metal" designates not a metallic powder, but a more or less cohesive metallic body derived from the powder by deformation, by heat-treatment, or by both these operations.

By analogy, we use the term "powder material" to designate cohesive bodies prepared from non-metallic powders.

To this group also belong non-metallic powders, free-flowing materials, soils, a considerable part of rock formations, and others. (Bodies with incomplete (partial) contact between particles can also be designated: by the index of individual deformability of the structural elements, as individually dispersed; by the index of porosity, as porous or non-compact; by non-continuity of contact, as bodies with non-continuous contact.)

Although these materials have a tremendous industrial importance, and most of them have been used since the days of antiquity, the theoretical studies and research pertaining to them, are just beginning to make some headway.

At present, it is this group of bodies with incomplete contact between their particles, to which, with more reason than to colloidal bodies, the famous appellation by V. Ostwald, "the world of forgotten magnitudes" may be applied. The study of this group of bodies, up to the present (in contradistinction to colloidal bodies) has not yet been segregated into an independent discipline.

Powder metallography, being a specific branch of general metallography, is at the same time a part of the science of bodies with incomplete contact [between their structural elements].

Many problems of metallography, as for instance, the crystallization of alloys, the distribution of stresses in the deformation of metals, etc., were studied on non-metallic materials. In studying the problems of powder metallography

it is also necessary to pay attention to research into non-metallic powder materials.

Powder metallography studies the structure and properties of metal powders and the powder metals derived from them, and also the changes in structure and properties during the process of obtaining the metal from the powder. Powder metallography is the theoretical foundation of powder metallurgy (metalloceramics), a branch of industry engaged in the manufacture of metal products from powders. Speaking scientifically, the operation of obtaining metalloceramic products from powders may be reduced to an increase in the contact between the particles. The increase in contact may be attained by two methods: (1) the deformation of the particles by external forces (pressing, calibrating); (2) the constriction of the metal atoms to the contact areas induced by the atomic mobility at increased temperatures. In practice, powder metallurgy utilizes both these methods (in any combination). Simultaneously with the increase in the contact surface of the particles, the toughness and the coherence of the powder metal become greater, and all its mechanical properties change.

It is for this reason that the study of contact phenomena is of exceptional importance to powder metallography. The most important assignments of powder metallography is the establishment of the following correlations:

- (1) The variations in the contact surface of the particles of the powder metal in relation to deformation (pressing, calibrating) and heat-treatment (baking).

(2) The variations in the structure and mechanical properties of the powder metal in relation to the size of the contact surface between its particles.

The Contact Surface

The contact surface is determined by the magnitude of the surface sections of contiguous bodies (particles), separated by intervals, the transverse dimensions of which are not in excess of the effective radius of the molecular forces. The mutual contact between the contiguous bodies (particles) may be either direct or accomplished through films of surface admixtures.

Strains and stresses both inside the bodies (particles), as well as from one body (particle) to the other may be transmitted with the aid of molecular forces only. Therefore, the above cited definition may be substituted by an equivalent one as follows: a contact surface is determined by the magnitude of surface areas, through which strains and stresses are transmitted from one contiguous body (particle) to the other.

The contact areas are in many cases the principal (at times, the only) gateways for the transmission of energy and the transmission of various processes from one body (particle) to the other. Thus, the transmission of an electric current from one metal to the other usually occurs at the places of contact. Thermal energy is most intensively transmitted from one body to the other through the contact areas. The processes of chemical interaction between solid bodies, in many cases

occur predominantly (and sometimes exclusively) through direct contact.

For a better understanding of contact phenomena in powders, it is necessary to study the same in compact bodies.

CHAPTER II

THE STUDY OF CONTACT PHENOMENA IN COMPACT BODIES3. The State of the Surface of Compact Metals

In a state of repose, the surface of liquids is smooth. In contradistinction, the surface of solids, even when polished to mirror-brightness, is always rough, due to numerous irregularities, projections, capillarities, and fissures of sub-microscopic, microscopic, and even macroscopic dimensions. Therefore, the area of the actual surface is in excess, by many times, of the area as measured geometrically.

Bowdan and Raydil (53) were determining surface areas, as accessible to hydrogen atoms. In the electrolytic precipitation of hydrogen on metallic surfaces, the amount of electricity required for a given increase in the electrode potential, was the same for all liquid electrodes, as, for instance, mercury, mercury amalgams, molten wood alloy, liquid gallium. In the case of solid metals, the above amount of electricity was considerably greater. On the basis of these measurements, a determination was made of the hydrogen-accessible metal surface areas, as shown in Table 1.

Table 1

Hydrogen-accessible surfaces of metals as per Bowden and Raydil

Surface	Ratio of accessible surface to apparent geometrical surface	Surface	Ratio of accessible surface to apparent geometrical surface
(Liquid mercury and other (liquid metals	1	(Nickel, activated by (consecutive oxidation (and reduction, fresh	46
(Wood alloy, solidified (shock-free	1.4	Same as above, but old	29
(Cadmium, solidified (shock-free	1.7	Freshly-pickled silver	51
Platinum, smooth foil	2.2	Old-pickled silver	37
Wood alloy, polished	6.3	Electric Arc Carbons	328-366
Nickel, recent polish	7.5	(Wood alloy, nitric (acid-pickled	800-1000
Nickel, old polish	9.7	platinum, platinized	1830

Table 1 shows that the accessible surface area of metals may be hundred and even thousands of times greater than the apparent geometrical surface. By comparing the data for freshly-treated and old-treated metals, it was established that the accessible metal surface was diminishing in the air due to the formation of oxides.

The magnitude of the hydrogen-accessible surface gives an indirect general idea about the presence of surface roughness and irregularities. A more direct evaluation of the amount, dimensions and configuration of these irregularities can be obtained by a profilometric study of the metal surfaces.

A detailed description of the various methods for the determination of the profiles of surfaces is contained in the books by Shmalts (71) and Shlezinger (70). For the purposes of metallographic examinations, the article is cut away normal to the surface, the section is ground, polished, pickled, after which the profile curve is photographed under a microscope. To avoid the distortion of the profile, a protective galvanoplated layer of copper or chromium (29), or a poured-on layer of an easily-fusible alloy, is placed on the surface prior to sampling.

In examining the surface under special profiling microscopes, the cutting of the article may be eliminated. (71) In this case, a narrow strip of light falls upon the specimen normal to its surface, while the observation is conducted along a different direction (most frequently parallel to the surface),

in which case the profile curve comes into view. Thus, as per the expression of Eppenstein ⁽⁷¹⁾, a "luminous cross-section" takes the place of the actual cross-section of the specimen surface. Figure 1, as per Shmal'ts ⁽⁷¹⁾, shows the microphoto of a steel surface by the method of luminous cross-section.

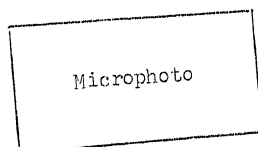


Figure 1. Surface of steel after planing (Shmal'ts) -- Magnified x 74.

Observation methods with the aid of a conventional metallographic or electronic microscope, that is permeable to the light of the surface relief replicas, were developed recently. For this purpose, a solution of a semi-transparent mass in a volatile solvent is applied to the specimen to be tested. Upon the desiccation of the solvent, the film is removed from the specimen, and the replica thus obtained, which is an impression of the surface relief, is observed in the permeating light under the microscope. The replica has its greatest thickness in the places corresponding to the concavities of the surface, and its smallest thickness in places corresponding to the protuberances. The concavities, therefore, appear darker-hued, and the protuberances, lighter-hued. Particularly good results are obtained by the study of the surface relief replicas under an electronic microscope, which allows the detection of roughnesses approximately down to the size of ten atomic layers. The recently de-

veloped method of "shaded metal platings" permits the detection of irregularities down to the size of 3-4 atomic layers⁽²³⁾. Figure 2 shows a photo of metal surface relief under an electronic microscope.

Microphoto

Figure 2. Electronic microphoto of the surface relief of aluminum (as per Genneberg)

Very satisfactory results can be obtained by measuring the surface profile with the aid of special profilographs. The design of most of the profilographs is based on the principle of the electric sound amplifier. A very thin needle, moving along the surface, feels its irregularities. The oscillations of the needle are magnified and recorded. Figure 3 (as per Beletskiy)⁽¹³⁾ shows profilograms of a series of surfaces. The magnification in a vertical direction is $\times 2000$, in a horizontal direction $\times 30$. Recently, the profilographs came into wide use in precision machine building for the quality control of the machined surface.

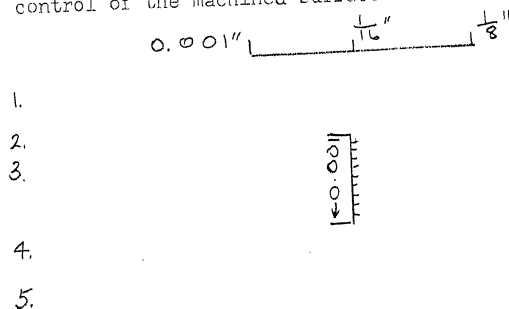


Figure 3. Profilograms (Beletskiy): 1. the mirror-like surface of

a cast-iron cylinder after finish-boring; 2. same after honing; 3. same after reaming; 4. the mirror-like surface of a worn automobile cylinder; 5. the mirror-like surface of a cast-iron cylinder after fine-boring.

Table 2 (as per Williamson and Abbott) cites the dimensions of the irregularities of finish-ground steel surfaces.

Table 2

Dimensions of the irregularities of finish-ground
steel surfaces (as per Williamson and Abbott)

<u>Types of Irregularities</u>	<u>Length of protuberance or convexity in microns</u>	<u>Height of protuberance or depth of convexity in microns</u>
Long protuberances and convexities	5000-12000	0.65
Short protuberances and convexities	750-1750	0.13-0.65
Sizable roughnesses	25-650	0.13-0.25
Fine roughnesses	5-10	0.025-0.13

Tables 3 cites the maximum dimensions of the surface protuberances and convexities after various types of machining.

Table 3

Maximum dimensions of irregularities of steel surfaces after various
types of machining, as per Moiseyev⁽⁴⁴⁾

<u>Type of machining operation</u>	<u>Height of protuberance or depth of convexity in microns</u>
Lathe turning	2.8
Finish-grinding	1.4
Honing	0.32
Lapping	0.13
Superfinish	0.025

Even the highest precision method of lapping of metallic surfaces, the method of superfinish, only recently adopted, results in irregularities of the order of magnitude of 100 atomic layers. Machining methods of a lower degree of precision result in protuberances and convexities of the order of magnitude of 10,000 atomic layers.

4. The Study of the Contact Surface

Due to the numerous irregularities, the actual surface of compact bodies is tens and hundreds of times greater than their apparent geometrical surface.

By the same token, the areas of actual contact of contiguous bodies constitute only an insignificant part of their apparent geometrical surface. The analysis of the profilogram presented in Figure 3 above makes it clear that bodies with

such a surface relief can be in contact at few points only. Under insignificant pressures, the surface is subject to little deformation, and the cumulative contact area amounts to one millionth of the total area. By the data presented by R. Holm⁽¹⁰²⁾, silver surfaces under the pressure of 0.0012 of a gram had a contact area of $12 \times 10^{-6} \text{ mm}^2$.

In some cases, the size of the contact surface can be determined visually, as in the case of contact between a sphere and a plane, between a cylinder and its intersecting axes, etc., if the pressure applied to the contiguous bodies is adequate for the formation of a deformation platform, the dimensions of which can be measured under a microscope. These determinations are made the same way as the measuring of the impressions in establishing the Brinell or Vickers hardness.

Some researchers now employ the visual surface determination by the Mekhau method⁽⁷¹⁾. The object under test is clamped under slight pressure against a quartz prism. At the place of contact with the prism, the reflection is disturbed, and the dark contact areas are visible against a brightly illuminated background. Yet, the Mekhau method shows not the actual contact areas, but the places of optical contact, i.e., places separated by intervals smaller than the length of a light-wave, the length of the latter being many times over the effective radius of the molecular forces.

The measuring of electrical conductivity permits the determinations of the contact surface at most insignificant pressures. In addition, in a series of cases, the emanation

of electrical conductivity furnishes a qualitative and even a quantitative concept on the state of the contact surface, the presence of admixture films, the thickness of these films, and the like. The absolute measurements of the contact area by electrical conductivity are possible when the number of contact areas are known (for instance, the contact between spheres, between a sphere and a plane, and between two intersecting cylinders). If the number of contact surfaces cannot be established (as in the case of the planes), only relative determinations are possible. The most substantial studies of contact phenomena by measuring electrical conductivity were published by R. Holm (102).

The determination of the magnitude of the contact surface by electrical conductivity is based on the following considerations (103). Let the contact between two bodies A and B (from the same metal, with a specific electrical conductivity λ), be effected on one circular platform, with the radius of the circle a , which is small as compared to the size of the body (Figure 4). In this case, the resistance of the bodies themselves may be disregarded on account of its significance as compared to the contact resistance. Thus, resistance and electrical conductivity are determined by contact resistance, which is made up of the following parts:

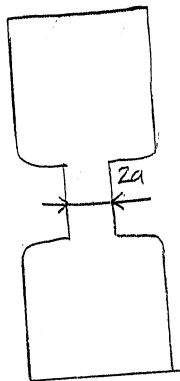


Figure 4. Contact between two bodies

1. Resistance, which is stipulated by the concentration of the lines of current at the passage from one body into the other across the narrow contact platform. This contact resistance is expressed by formula, the derivation of which is outlined by Holm⁽¹⁰²⁾:

$$R_k = \frac{1}{2a\lambda}$$

(4/1)

Holm calls this resistance the "screen resistance", by analogy with the resistance in the passing of water through a screen with very narrow holes. For the complete analogy, the screen is to be visualized as having an infinitesimally small thickness. This part of the resistance may be called purely metallic resistance.

2. Intermediate resistance $\ddot{u}$ (Übergangswiderstand), stipulated by the passing of the current through the narrow contact layer, containing admixtures, with a cross-section area πa^2 and thickness y (see Figure 4).

If this layer is filled completely with the film of admixtures having an electrical conductivity λ , then

$$\ddot{u} = \frac{y}{\pi a^2 \lambda_s} \quad (4/2)$$

If the layer of admixtures is not continuous, then

$$\ddot{u} = \frac{f(y)}{\pi a^2} \quad (4/3)$$

where $f(y)$ is the function of the thickness of the admixture-enriched layer.

Footnote. Holm disregards the intermediate resistance of this thin layer, when it has no admixtures. This intermediate resistance $\frac{y}{\pi a^2 \lambda}$, considering the insignificant value of thickness y and the high electrical conductivity of the pure metal, can always be disregarded by comparison with the screen resistance $R_R = \frac{1}{2a\lambda}$.

It follows from formulas (4/2) and (4/3) that $\ddot{u}$ is in direct ratio to $\frac{1}{a^2}$, and, therefore, with the growth in the size of the contact platform, it loses its significance as compared with R_R , which is in direct ratio to $\frac{1}{a}$.

Holm's experiments have shown that by simply cleaning the contacts (pickling and degreasing the surface, scraping the surface layer), the admixtures have little effect on the contact resistance which is basically determined by its pure metal part as per formula (4/1). In a contaminated contact, the intermediate resistance of the admixtures may be very high. The fact that the resistance in the case of cleaned contacts is in series of cases purely metallic, and that the intermediate resistance, as per formulas (4/2) and (4/3), may be disregarded, is confirmed by the following data:

1. The size of the contact surface, as computed by formula (4/1), coincides with its size, as determined visually (see paragraph 6).

2. With temperature, the contact resistance will vary in a ratio characteristic for the metal, but not for the admixtures.

3. With temperatures approximating absolute zero, the contacts have manifested, in some cases, phenomena of superconductivity, which would have been impossible in the presence of continuous admixture films.

In the general case, in the presence of one contact platform of any shape, the ratio between the magnitude of the contact surface and the contact electro-conductivity (without taking into account the intermediate resistance) is expressed by the following formula:

$$\lambda_R = \frac{1}{R_R} = K \lambda \sqrt{A}, \quad (4/4)$$

where λ_R is the contact electro-conductivity (purely metallic), R_R is the purely metallic contact resistance, K is a constant numerical coefficient, λ is the specific electro-conductivity, A is the contact surface.

Footnote. More precisely, not the contact surface itself, but its projection upon the area of separation between contiguous bodies.

5. Interatomic Forces. Forces of Surface Cohesion. Equilibrium between External and Interatomic Forces

Crystalline solid bodies have a regularized structure. The atoms, molecules, or ions of the crystalline solid body are disposed in a definite order at appropriate distances from one another, forming the so-called spatial lattice. The lattices, with relation to the disposition at their junctions of atoms,

ions, or molecules, are divided into atomic, ionic, or molecular lattices. Metals form atomic lattices.

Molecules (atoms, ions) are held at the lattice junctions by electrical forces of attraction and repulsion. These electrical forces are considerably greater than the gravitational forces. For instance, the electrical attraction between the ions of sodium and chlorine is 10^{33} times greater than the gravitational attraction between them.

Electrical inter-action forces between the atoms are in an inverse ratio to a predetermined degree of remoteness between them, it being the case that the forces of repulsion diminish with distance much more rapidly than the forces of attraction. In the case of haloids, attraction between the ions diminishes with the square of the distance, while repulsion between them diminishes with the 9th power of the distance. According to G. Mie⁽¹²⁵⁾, the force of interaction between two atoms (molecules, ions), in relation to the distance between them, is expressed by the formula:

$$P = \frac{a}{r^m} - \frac{b}{r^n} \quad (5/1)$$

where P is the resultant force, r is the distance between the atoms, a, b, m, n are constant values (dependent on the type of atoms), it being the case that $m > n$.

In this equality, $\frac{a}{r^m}$ represents the force of attraction, $\frac{b}{r^n}$, the force of repulsion. The algebraic sign of the resultant force is determined by one of the component forces being

in excess of the other.

The effect of the forces of repulsion increases with temperature. To take account of this factor, it is necessary to introduce into equality (5/1) a third term with a minus sign:

$$P = \frac{a}{r^m} - \frac{b}{r^n} - \frac{c(T)}{r^l} \quad (5/2)$$

where $c(T)$ is a certain function of the absolute temperature, which increases with the increase in the latter,

l is a constant.

Figure 5 is a graphic representation of the ratio between the resultant force P and its individual components, on the one hand, and the distance between the atoms at a predetermined temperature, on the other hand. The curve (1) represents the above ratio for the force of attraction $\frac{a}{r^m}$, curves (2) and (3), for the forces of repulsion $\frac{b}{r^n}$ and $\frac{c(T)}{r^l}$, curve (4) for the resultant force.

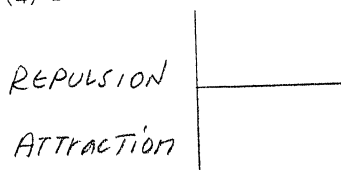


Figure 5. Ratio of interatomic forces to interatomic distance
(as per Mie)

In a non-deformed crystal, which is not subjected to the effect of external forces and in which internal stresses are absent, the distance between the atoms in the atomic lattice r_a (see Figure 5) conforms to a state of equilibrium

between the forces of attraction and repulsion ($P = 0$). External forces applied to a solid body deform the atomic lattice and are counterbalanced by the interatomic forces. In compression, the interatomic intervals are decreased, and the forces of repulsion begin to predominate, to the effect of balancing off the external pressure and transmitting it to the following layers of the atomic lattice. When the external pressure is removed, the interatomic forces of repulsion restore the original distance between the atoms in the cells of the lattice. In tension, the distance between the atoms is increased, and the evolving forces of attraction tend to draw them closer. Thus, interatomic forces, in constantly tending to restore the disturbed equilibrium, are constantly of an elastic nature. The transmission of the effect of the external forces in the direction of their line of application is also due to the elastic character of the interatomic forces.

It must be emphasized that the interatomic forces retain their elastic characteristics also under plastic deformation, and that plastic deformation is always accompanied by elastic deformation. In elastic deformation, only the distance between the atoms, but not the order of their disposition, is changed. In the case of elastic deformation, as soon as the external forces are removed, the atoms return to their initial locations. In plastic deformation, which is always accompanied by elastic deformation, not only the intervals between the atoms, but also the order of their disposition, is changed. Upon the removal of the external forces in plastic deformation, the new order of atomic disposition remains, but the initial distances between

the atoms in the lattice cells are restored (inasmuch as it is not hindered by the formation of residual stresses). In the presence of residual stresses, such interatomic distances are established as will permit the counter-balancing of the residual stresses by the interatomic forces.

Under the effect of an elongating force, as shown in Figure 5, the balancing resultant force of attraction increases to a maximum value P_m , which is conformant to the distance between the atoms r_m . After this, the value of the force of attraction begins to diminish. Therefore, when the external elongation forces become greater than the P_m value, the atoms may move to distances beyond the effective sphere of interatomic forces, and a tensile break will occur. The technical value of tensile strength is many times below the theoretically computed values of P_m , which is due mainly to plastic deformation, and, at times, to structural defects in the actual crystals.

The external forces are counterbalanced and transmitted by the interatomic forces not only inside a solid body, but also from one solid body to another. All the external pressure can be transmitted from one body to the other through the surface contact areas only. Stresses cannot be transmitted through any other surface areas, since they are located beyond the sphere of interaction of the molecular forces of both surfaces. Hence, the contact areas are locations of a considerable concentration of stresses.

The atoms in the internal layers of the crystalline lattice are surrounded on all sides by other atoms which counter-

balance the electrical forces of attraction of the former. The atoms in the surface layer of the crystal are in a different position, since part of the electrical forces is not counter-balanced. Hence, the dimensions of the crystalline cells in the surface layer of the lattice are somewhat distorted. In metals, according to Yum-Rozeri, there occurs an expansion of the lattice at the surface layer; in ion crystals, according to Leonard-Jones, on the contrary, there is surface shrinkage. The interatomic distances at the ribs and in the corners of the crystals are distorted to an even greater extent. Due to the non-saturation of the surface electrical forces, the atoms of the surface layer can attract the atoms or molecules of solid, liquid, or gaseous substances (the phenomenon of so-called adsorption). These non-saturated surface forces are known as the forces of surface cohesion.

Let us visualize two cube crystals of the same substance with simple cubic lattices of the same orientation and with ideally flat surfaces parallel to the plane of the lattice cube. Let us draw the cube crystals close to one another so that the atoms in their surfaces are similarly disposed (Figure 6)

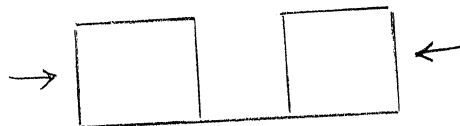


Figure 6. Contact in bringing together two similarly-oriented crystals.

When the distance between the surface atoms will equal the constant of the lattice l_0 , both crystals will merge into

one. It is perfectly clear that, in order to break the contact between the surfaces in this case, a strain of the same magnitude as it will take to break the bond between the atoms inside the crystal, will be required. This example shows that the forces of surface cohesion do not have to differ in magnitude from the forces of interatomic bond inside the crystallites of a body. The experiments by Holm, which demonstrated that the resistance to the breaking of contacts between pure metallic surfaces constitutes a magnitude of the same order as the temporary tensile strength, may serve as a confirmation of this assumption.

For the proper understanding of the mechanics of the effect of the forces of cohesion, it must be emphasized that these forces do not induce the drawing together of the solid bodies or particles, but only fix the bond between the surface layers at the already existing areas of contact. The forces of cohesion induce the shifting of atoms or molecules, but not of solid bodies or particles. At low temperatures, the forces of cohesion cannot increase the surface contact between solid bodies, while at high temperatures, such an increase, as described in Chapter IX, is due not only to the direct effect of cohesion, but also to the thermal oscillations of the atoms (molecules).

Under usual conditions, surface admixtures are always present in solid bodies. The presence of these admixtures is, to a considerable extent, due directly or indirectly to the effect of the forces of cohesion. The forces of cohesion

indirectly promote the formation of oxidation films, since the adsorption of oxygen is a requisite preliminary condition for oxidation.

The effective radius of the forces of cohesion, as is shown by the study of adsorption phenomena, constitutes a magnitude of an order somewhat in excess of one atomic layer.

6. Deformation of Contact Surface. The Ratio between the Contact Area and Pressure

The contact surface is increased as a result of deformation under pressure, normal to the surface of separation of contiguous bodies. As a result of extensive research, there is now available a substantial amount of data, which, to some extent, clarifies the problems and supplies answers to the following questions on the nature of deformation of the contact surface:

(1). What are the mechanics of the formation of the contact surface in deformation? Is this deformation reversible or non-reversible?

(2). What is the quantitative ratio between the contact surface area and pressure?

(3). Does the formation of a new contact surface take place by way of increasing the size of the already existing contact areas or by way of developing new contacts?

(4). What is the effect of surface admixtures on the formation of a contact surface in deformation?

Some researchers, as, for instance, Tomlinson, Kontorova,⁽³²⁾

maintain that the sections contiguous to the contact surface, are subject to elastic deformation. In the opinion of others, such as Holm⁽¹⁰²⁾, Bowden and Tabor⁽⁸³⁾, the places of contact are subject to plastic deformation.

Due to surface irregularities, the contact between bodies can be effected only through small protuberances, the bearing area of which (A), in the absence of pressure, approximates zero. Let two bodies, under pressure P, normal to the surface of separation between them, be contiguous through supporting contact protuberances (as shown in Figure 7).

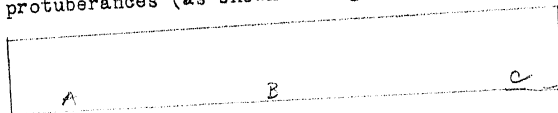


Figure 7. Contact surface deformation diagrams.

Let us assume that the boundary between the supporting contact platforms coincides exactly with the plane of separation between the contiguous bodies, i.e., normal to the applied pressure (see Figure 7,a). If surface A of the supporting platforms is very small, and force P very great, the actual specific pressure upon the contact areas $\frac{P}{A}$ will be in excess of the critical stress σ_k , at which the plastic flow of the material begins. The growth of the contact surface of the protuberances, induced by this plastic deformation, will continue until such time as the stress in the supporting platforms is reduced to the critical value σ_k :

(6/1)

$$\begin{aligned} \text{or} \quad \sigma_k &= \frac{P}{A} \\ A &= \frac{1}{\sigma_k} P \end{aligned} \quad (6/1a)$$

Actually, the contact surface almost never coincides with the plane of separation normal to the acting force P (Figure 7, b and c). It is clear that the strength of the contact protuberances does not depend on the profile of the boundary and the real magnitude of the actual contact surface A , but is determined by the transverse section of the protuberances, i.e. by the magnitude of the projection of the contact surface upon the plane of separation, normal to the applied pressure. Then:

$$\sigma_k = \frac{P}{A_n} \quad (6/2)$$

or

$$A_n = \frac{1}{\sigma_k} P \quad (6/2a)$$

In all further analysis, when deformation of the contact surface is mentioned, it is specifically the projection of the contact surface upon a plane normal to the acting force that is meant. For brevity, it would be appropriate to introduce a special term for the designation of this magnitude, as, for example, the conditional contact surface, or the effective contact surface.

In many cases, the most suitable, in our opinion, are the terms "the contact cross-section" and "the contact cross section area", since this projection is equal to the cross section of the contact protuberances, normal to the acting force.

In further text, we shall use the latter term as well as the expressions "contact surface" and "magnitude of contact surface", bearing in mind that these terms pertain not to the actual surface, but to its projection.

The non-reversible deformation of the contact areas, in a number of cases, may be not only plastic, but also brittle. For instance, a piece of coal or chalk will leave an impression on paper even under the effect of its own weight, which is obviously due to the breaking off of their particles at the place of contact. The formulas (6/2) and (6/2a) prevail also in this case, if σ_R is considered as the critical strength, with the protuberances breaking when it is exceeded, until supporting platforms are formed to such a magnitude that the pressure upon a unit of the projection area is diminished to equal the critical magnitude σ_R .

The value of the critical stress ("contact toughness") σ_R is closely linked to the hardness of the material. From formula (6/2) it follows that σ_R equals the pressure requisite for the obtaining of a contact surface, the area of the projection of which upon a plane normal to the acting force equals unity. In the determination of hardness by the methods of Brinell, Vickers, or Meyer (the Meyer method is described by O'Neil⁽⁴⁷⁾), the impression left by pressing in the steel or diamond ball, or cone into the softer material that is being tested, is essentially the contact surface between them. The Brinell and Vickers hardness in this case equals the pressure in kilograms that it takes to form a unit of area (1 square millimeter) of the surface of contact with the material being

tested. The Meyer hardness equals the pressure in kilograms that it takes to form a section of contact with a projection area of 1 square millimeter. The Meyer hardness determines the "contact toughness" of the material in the same manner as does the critical stress σ_R . Hence, the critical stress of the softer material σ_R , expressed in kilograms per square millimeter, coincides with its Meyer hardness, H_M . The values of σ_R and H_M also coincide in the case of contact of two bodies of the same hardness. The Meyer hardness is somewhat greater than the Brinell and Vickers hardness (usually by 5 to 20 percent). Table 4, as per Holm, shows that in the case of contact between homogeneous metals, the critical stress σ_R is not much different from the Brinell hardness value.

Table 4

The value of the critical stress σ_R for various metals,
as per Holm

Metal	Load on contact in kilograms	σ_R in kg/sq mm	Metal	Load on con- tact in kilograms	σ_R in kg/sq mm
Lead	3	2.3	Platinum	3	78
Bismuth	3	3.8	Platinum	15	74
Tin	3	4.5	Nickel, va-	12	83
Antimony	3	10.6	cuum annealed		
Graphite	15	13.2	Tantalum,		
Silver	6	31	soft	15	90
Copper	6	39	Tantalum,		
Zinc	3	43	hard	15	250
Gold	15	53	Molybedum	15	169
			Tungsten	21	372

If the critical stress σ_k and the Meyer hardness, H_M of the material were constants, completely independent of pressure, the contact surface, as indicated by formulas (6/2) and (6/2a) would vary in direct ratio to pressure. In a limited range of pressures, as will be indicated below, there really is an approximately direct ratio between pressure and the contact surface. Generally speaking, however, σ_k and H_M are not constants, but are increased with pressure, due to the toughening of the material. Hence, in great ranges of pressures, A_n increases in direct ratio not to the first degree of pressure, but to a somewhat lesser degree.

A look at the surface profile of a solid body (see Figure 3) shows that an increase in the area of contact surfaces with protuberances to 10,000 atomic layers requires a change in the order of atomic disposition, i.e. a non-reversible deformation, plastic or brittle. This is confirmed by fact as described below

(1). Ratio between the magnitude of the contact surface and pressure

In the elastic contact between a sphere and a plane, two spheres, or intersecting cylinders, the contact area (or, more precisely, the projection of the contact area upon the plane of separation between the contiguous bodies) is, according to Gerts, proportional to normal pressure raised to the power of $2/3$

$$A_n = c P^{\frac{2}{3}} \quad (6/3)$$

where c is a constant numerical factor.

According to formula (4/4), the contact electro-conductivity is in direct ratio to the contact surface raised to the power of $1/2$:

$$\lambda_R = \frac{1}{R_R} = K \lambda A_H^{\frac{1}{2}},$$

where λ_R is the contact electroconductivity,

R_R is the contact resistance,

λ is the specific electroconductivity

K is a constant coefficient

Combining formulas (6/3) and (4/4), we derive:

$$\lambda_R = \frac{1}{R_R} = K_1 P^{\frac{1}{3}} \quad (6/4)$$

where K_1 is a constant coefficient, i.e. in elastic deformation electroconductivity is proportional to pressure raised to the power of $1/3$.

Combining formulas (6/2) and (4/4), we derive:

$$\lambda_R = \frac{1}{R_R} = K_2 P^{\frac{1}{2}} \quad (6/5)$$

where K_2 is a constant factor, i.e. non-reversible deformation electroconductivity is in direct ratio to pressure raised to the power of $1/2$.

Research by a number of scientists, such as Holm⁽¹⁰²⁾, Kontius, Bowden and Tabor⁽⁸³⁾, revealed that contact electroconductivity is in direct ratio to $P^{\frac{1}{2}}$, and not to $P^{\frac{1}{3}}$; hence, deformation of contact areas is non-reversible.

Data by Bowden and Tabor⁽⁸³⁾ pertaining to contact between intersecting steel, copper, and silver cylinders is given in Table 5.

TABLE 5

Ratio between Contact Surface and Pressure for
Steel and Silver Contacts (as per Bowden and Tabor)

Metal	Pressure upon contact in kg	Contact surface (in cm ²)		
		by electro- conductivity	visual	computed by σ_R
Steel	1	0.00013	--	0.0001
	5	0.00061	--	0.0005
	50	0.0045	0.0045	0.005
	500	0.042	0.045	0.05
Silver	0.5	0.0002	--	0.0002
	5	0.002	--	0.002
	50	0.018	0.019	0.02
	500	0.15	0.19	0.2

Note -- Steel contacts: cylinder radius $r = .5 \text{ cm}$;
critical stress inducing the flow of the material σ_R
= 100 kilograms per square millimeter, specific electro-
conductivity $\lambda = 75,000$ centimeters per ohm. Silver contacts:
 $r = 0.45 \text{ cm}$; $\sigma_R = 25 \text{ kg/mm}^2$; $\lambda = 620,000 \text{ cm/ohm}$.

The dimensions of the contact surface as determined

by various methods -- visual, by electroconductivity, and by the theoretical computation of plastic deformation, show rather good coincidence.

Experimental data confirm the existence of a direct ratio between the contact surface magnitude and the pressure. Holm's experiments lead to the assumption that even in the presence of very insignificant loads, like one thousandth of a gram, the contact areas are subject to plastic deformation, it being the case that the area stresses are magnitudes of the same order as in the presence of high pressures.

Some departures from the linear ratio between the pressure and the contact surface projection with an increase in load are due to the increase in the critical stress σ_k caused by the cold-hardening of the material. Table 6, compiled by the author from the Bowden and Tabor data in Table 5, clearly indicates the increase in pressure per unit of contact surface with load application.

TABLE 6

Ratio between Contact (Critical) Pressure σ_k and Load

Load on contact in kilograms	Contact pressure σ_k in percent	
	Steel contacts	Silver contacts
0.5	--	100
1	100	--
5	107	100
50	144	111
500	155	133

Note. The correct pressure was computed by electro-conductivity.

(2). Phenomena of Friction

The ratio between force f , requisite for the overcoming of friction, and the normal load P (see Figure 8) is expressed by the Amonton-Coulomb law as follows:

$$f = \mu P \quad (\epsilon/6)$$

where μ is the constant coefficient of friction.

The above law is easily understood, if the existence of plastic (or brittle) deformation of the contact surface and the direct ratio between pressure and the contact surface projection are assumed. However, it does not follow from an elastic contact, as per formula (6/3).

From the experience with bearing operation it is well known that, even in the presence of very small loads, friction is accompanied by non-reversible deformation -- plastic (the bearing surface run-in) and brittle (bearing wear). The surface profilogram of a worn automotive cylinder (see Figure 3) clearly shows the smoothening of the protuberances as a result of the surface run-in.

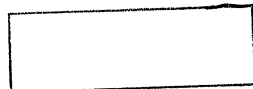


Figure 8. Normal load and the force of friction

The static coefficient of friction μ_s is always greater than the kinetic coefficient μ_R . The static coefficient of

friction is computed on the basis of measuring the force requisite to impart a sliding motion to a body in repose, and the kinetic coefficient of friction, on the basis of the force requisite to sustain the sliding of a body already in motion. The greater magnitude of the static coefficient of friction is due to the fact that it takes some time for the plastic deformation to take effect, as a result of which bodies at rest have a somewhat greater surface area than bodies in motion.

In summarizing, we note:

- (1) The increase in the contact area under load is linked with a non-reversible deformation in the contact area, plastic and brittle.
- (2) The load, if toughening is disregarded (see Table 6), induces not an increase in pressure per unit of the contact area projection, but an increase in the contact surface. The actual pressure per unit of the contact area projection (the critical pressure σ_R) is approximately the same under low as well as high pressures, and equals the Meyer hardness of the material. Thus, the contact surface is always under stress.
- (3) The area of the projection of the contact sections upon a plane normal to the pressure (contact cross-section), if the effect of toughening is disregarded, increases in direct ratio to the load. In essence, this ratio follows directly from the determination of the contact surface in preceding paragraph 2.

7. The Mechanics of the Formation of a Contact Surface. Further

Data

The study of contact electroconductivity reveals that during deformation, a new contact surface is formed by the increase in the already existing contact sections or by formation of new contact places.

If the area of already existing places of contact is increased with pressure, electroconductivity will increase in direct ratio to the square root of the load (see paragraph 4):

$$\lambda_k = k P^{1/2}$$

Research by Holm, Kontius, Bowden and Chel'khlin revealed that, when the geometrical contact between bodies is effected at one or several predetermined points (such as: between two intersecting cylinders), specifically such a ratio between electroconductivity and pressure is observed. Consequently, in these cases, the contact increases with pressure by an increase in the already existing contact sections, as is also confirmed by visual determinations.

In the case when the load induces the formation of new contact sections in numbers proportional to the pressure (contact area), electroconductivity must increase in direct ratio to the first degree of pressure:

$$\lambda_k = k P$$

Such a ratio is observed frequently when the apparent geometrical contact is to be effected along an unbroken surface, as between two plates, between bolt and nut, and the like^(83, 102). Seemingly, in these cases, the number of contact section increases in direct ratio to the load.

Footnote. In the opinion of the author, this confirms once more the non-reversible nature of the contact surface deformation. Under conditions of plastic deformation, the formation of a contact surface at new points of the plane, due to the toughening of the previous contact sections, is more probable. Under conditions of elastic deformation, it would be rational to expect, in addition to the formation of new contact sections, an increase in the already existing sections of contact, and electroconductivity would increase to a lesser extent than with the first power of P .

Sometimes, in the case of contact between flat surfaces, electroconductivity will increase in direct ratio to the load raised to the power of 0.9. It may be that, in these cases, the pressure simultaneously induces both an increase in the already existing contacts, as well as the formation of new contact sections. Other explanations, however, are possible.

The surface layers of metallic bodies are always contaminated with admixtures. Hence, the visual determination will always result in somewhat greater values for the areas of contact than the electrical determinations (see Table 5). Generally speaking, there may be two cases of the surface ad-

mixture effect upon the contact surface-pressure ratio.

In the first case, the admixtures are either non-stable or in insignificant amounts, and, therefore, do not affect the magnitude of the contact surface of bodies at rest (Footnote: Under a contact surface we understand surface sections, which transmit stresses from one body to another. It is clear that, in all cases, the presence of any admixtures will decrease or even completely eliminate the fraction of the purely metallic contact between bodies). For instance, visual (but not electrical) determinations revealed that surfaces at rest, when lubricated with oil, have the same contact area as non-lubricated surfaces.⁽¹⁰²⁾ This is due to the fact that the size of the pressure-transmitting contact platforms are, in this case, determined entirely by the toughness of the metal, and not by the toughness of the lubricant film. Such low-strength or brittle films may be partly, or even entirely, pressed out or disintegrated under the effect of pressure. R. Holm, Guldenpfenning, E. Holm, and Stermer conducted a 150-time test of loading and deloading of nickel contacts covered with unbroken films of oxide. As a result of the disintegration of the oxide films, electrical resistance decreased ten-fold, it being the case that its last value was equal to the purely metallic resistance. Similar results were obtained with the use of oil films.

In the second case, the admixtures are so stable and their amount so considerable that the dimensions of the contact surface are, to some degree, determined by their tough-

ness, and not by the toughness of the metal proper. Holm, for instance, observed a considerable increase in the critical stress under very small loads, on the order of 0.001 of a gram. Khrushchov and Berkovich⁽⁶⁸⁾, in studying micro-hardness, discovered that, for micro-impressions of approximately 10 μ , hardness decreases with pressure.

The author explains this phenomenon by the increased hardness of many surface oxides as compared to the hardness of the basic metal, such as aluminum oxide, corundum. Under low pressures, the volume of the hard admixtures is subject to deformation (see Figure 9), and, therefore, the size of the contact surface per unit of load is smaller than under high pressures when the softer pure metal is subject to deformation. However, even in these cases, the pressure may lead to the formation of a purely metallic contact, since the admixture layer is always more brittle than the basic metal.

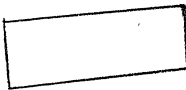


Figure 9. Contact in the presence of surface admixtures:
1. under low pressure; 2. under high pressure.

The Work Involved in the Formation of a Contact Surface

In some cases, as in the contact between a hard metal cone and a softer metal flat surface, the work involved in the formation of a contact surface, may be determined. The pressure, P , induces a plastic deformation not in the cone,

but in the softer flat metal, in which the cone, in penetrating to some depth h , leaves a corresponding imprint. (Figure 10). In so doing, the cone is intersected by the plane along a circle of diameter D , the area of which $\frac{\pi D^2}{4} = A_n$ is equal to the projection of the contact surface upon a plane.



Figure 10. The pressing in of a cone.

The work W , involved in the formation of a contact surface, is in this case connected with the pressing out of the volume of metal occupied by a cone with an apex angle φ , height h , and diameter D , and is equal:

$$W = \int_0^h P dh = \int_0^A \sigma_k A_n dh = \sigma_k \int_0^{A_n} A_n d \frac{D}{2 \tan \varphi/2}$$

$$= \frac{\sigma_k}{2 \tan \varphi/2} \int_0^D \frac{\pi D^2}{4} dD = \frac{\sigma_k \pi}{24 \tan \varphi/2} D^3 = \frac{\sigma_k}{3 \tan \varphi/2 \sqrt{\pi}} A_n^{1.5} \quad (8/1)$$

Thus, the work involved in the formation of the contact surface, in this case, is in direct ratio to the projection of the contact surface raised to the power of 1.5.

It follows from formula (8/1) that, given the same size of A_n , the work involved in the formation of a contact surface for various metals is in direct ratio to the value of σ_k .

Substituting $\frac{P}{\sigma_k}$ for A_n in formula (8/1), we derive:

(8/2)

i.e. under equal pressures, the work involved in the formation of a contact surface, in the case of various metals, is in an inverse ratio to $\sqrt{\sigma_R}$.

In the case of contact between a cone and a plane, there is the formation of an unbroken surface of osculation, which grows by the increase of one contact section. In this case, the work involved in the formation of the contact surface is in direct ratio to the magnitude of the latter raised to the power of 1.5, since the deformed volume increases more rapidly than the area of osculation.

If, as a result of pressure, the previous contact surface sections are not increased, but new ones are formed instead, in a number that is in indirect ratio to the magnitude of the contact surface.

Change in the Magnitude of the Contact Surface with the Removal of Load. The Elastic Aftereffect

As indicated, the contact surface is always "stressed". The external pressure is counterbalanced at the contact sections by the interatomic forces, the resultant of which is equal and opposite to the force applied. When load is removed, the interatomic forces are no longer counterbalanced, and they will produce deformation in a direction opposite to deformation under load. This phenomenon is known as the elastic aftereffect.

Let us now analyze the case of contact (pressing-in) between a hard ball and a softer flat plate, as occurs in the

Brinell hardness determination (Figure 16). Pressure, P , induces stresses, the sum of which equals minus P in a direction normal to the surface of the plate, and considerably lesser stresses in the direction of the surface. When load is removed⁽⁴⁷⁾, the elastic aftereffect promotes the so-called restoration (Figure 11b), which is expressed in a considerable reduction of the depth of the impression (in this direction, the internal stresses were of the maximum value) and in a not so noticeable reduction along the diameter (the direction of the minimum internal stresses). Conformantly, as per data by Foss and Brumfield⁽⁹¹⁾, very considerable distortions were observed in the determination of hardness by the depth of the restored impression (from 1 to 250 percent), while in determinations by the diameter of the impression, the distortions, on the contrary, were insignificant (from 0 to 2 percent).

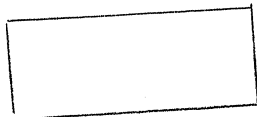


Figure 11. Elastic restoration: a. non-restored; b. restored impression

Table 7 (as per Foss and Brumfield)⁽⁹¹⁾ clarifies the effect of the elastic aftereffect upon the restoration of impressions obtained in Brinell hardness determinations in various materials. It shows a clearly pronounced increase in elastic aftereffect with increased hardness of the material.

TABLE 7

The Elastic Aftereffect as Manifested in the Distortion of the
Curvature of the Impression of a 10-Millimeter Steel Ball
 (as per Foss and Brumfield)

Specimen	Brinell hardness in kg/mm ²	Diameter of ball in mm	Diameter by the re-stored impression, in mm
Soft bronze	90	10	10.10
Cold-hardened bronze	151	10	10.61
(Steel (1.5% Cr, (0.3% V, 0.4% C):			
after normalizing	318	10	13.87
after hardening	758	10	27.60
(Steel (3.5% Ni and (0.5% C) after harden-			
ing	605	10	23.06
Steel (0.95 C) after			
hardening	774	10	34.64

Table 8 presents the data by O'Neil relating to the effect of the elastic secondary action upon the restoration of the depth of the impression, when the load is removed. Tables 7 and 8 permit the conclusion that the elastic aftereffect may cause deformation sufficient for the disruption of the contact.

TABLE 8

The Effect of the Elastic Secondary Action Upon the Restoration
of the Depth of the Impression (as per O'Neil)

Load in kilograms	The depth of the non- restored impression		The depth of the re- stored impression	
	μ	%	μ	%
92	50	100	29	58
112	60	100	37	61
141	70	100	46	66
166	80	100	55	69
200	90	100	64	71

Whether the elastic aftereffect, after the removal of the load, induces a complete or only a partial disintegration of the contact surface, depends on a number of causes. Table 9 presents data relating to the elastic deformation of the contact sections, which is characterized by the ratio of the contact stress σ_R to the modulus of elasticity E . Table 9 has been compiled by the author on the basis of data by Holm⁽¹⁰²⁾ relating to σ_R value and data by Landolt-Bernstein relating to the value of E .⁽¹¹⁹⁾ It can be seen from Table 9 that hardness and the critical stress, σ_R (the numerator of fraction $\frac{\sigma_R}{E}$) increase more rapidly than the elasticity modulus E (the denominator of the fraction $\frac{\sigma_R}{E}$). Thus, the value of σ_R for tungsten is 160 times greater than for lead, and the elasticity modulus is 23 times greater. There-

fore, the elastic deformation of the contact sections of tungsten is 7.4 times greater than the same of lead. It is also obvious that the effect of the elastic secondary action in the case of toughened metal is greater than it is in the case of soft metal, since in this case the value of σ_R increases, while the value of E does not change.

TABLE 9

Elastic Deformation in Contact Sections

Metal	Critical stress		Modulus of		Elastic deformation in	
	σ_R		elasticity E		contact section σ_R/E	
	arbitrary		arbitrary		arbitrary	
	kg/mm ²	units	kg/mm ²	units	%	units
Lead	2.3	1	1600	1	0.14	1
Silver	31	13.5	8000	5	0.39	2.79
Platinum	74	32.2	16000	10	0.46	3.29
Tungsten	372	162	36000	22.5	1.03	7.36

If we assume that the contact was being effected through the protuberances from 200 to 2000 atomic layers in length, then, in conformity with Table 9, we will have the elastic deformation of unloading from 0.3 to 2.8 atomic layers, in the case of lead, and from 2.1 to 20.6 atomic layers, in the case of tungsten. Thus, after lead is removed, a part of the surface atoms of lead remain in the contact (i.e., in the sphere of interaction of the atomic forces), while the tungsten atoms are drawn out of the contact.

Footnote. The above argumentation is helpful in understanding the underlying reason behind the fact that, in the case of the Johanson gage blocks (surface irregularities on the order of 100 atomic layers), even insignificant pressures produce a much tougher contact than in the case of roughly-machined surfaces with irregularities of the order of 10,000 atomic layers. However, in the presence of higher pressures, the rough surfaces will adhere better, due to the mutual wedging-in of the surface protuberances (similar to the wedging-in of the axe in a log of wood).

Whether the contact will be broken with the removal of the load, depends to a great extent on the contact toughness, which problem will be treated in paragraph 10.

With the application of a load, the projection of the contact surface varies in direct ratio to pressure. When load is removed, it does not result in a uniform ratio between the contact area and pressure for all cases.

Let a body under pressure P_1 rest upon a contact platform A_n . When the load is increased from P_1 to P_2 , A_n increases in direct ratio to the pressure along the straight line B_1B_2 (Figure 12), in which point B_1 corresponds to pressure P_1 and contact surface A_{n1} , B_2 corresponds to the coordinates A_{n2} and P_2 . Let us now reduce the pressure to its initial value P_1 . In removing the load under these conditions, three variants pertaining to the change in the contact surface may occur.

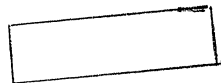


Figure 12. Changes in the contact surface under conditions

of loading and unloading.

In the first case, there is a fully-reversible ratio between A_n and pressure (Figure 12,a). The change in A_n under load occurs along the straight line B_2B_1 , and, at the end of the cycle, with the initial pressure P_1 , it reverses to the initial point B_1 . Let us introduce the term residual surface conceiving under it the difference between the contact surface at the beginning and at the end of the cycle. In this case, the residual contact surface equals zero.

In the second case (Figure 12,b), the contact surface, when load is removed, retains at all times the value A_{n2} , which was attained at point B_2 . Therefore, the ratio between the contact area and pressure is determined by the straight line $B_2B'_1$, parallel to the X-axis. In this case, the residual contact surface A_0 , which is expressed by the cut-off B'_1B_1 , has the maximum possible dimension, equal to $A_{n2} - A_{n1}$.

In the third case (Figure 12,c), when load is removed, the contact surface is decreased along the curve $B_2B'_1$ lying above the straight line B_2B_1 , but below the straight line B_2A_{n2} . In this case, some part of the osculation surface, formed under load, remains. The residual surface A_0 , expressed by the cut-off B'_1B_1 , equals $A'_{n2} - A_{n1}$, where $A_{n2} > A'_{n2} > A_{n1}$.

It should be noted that the residual surface is also a

"stressed" surface, since the presence of residual contacts is due to the existence of residual stresses, which equal σ_R (per unit of contact area).

Research into contact conductivity undertaken by Holm and his collaborators, revealed that, when the load was removed, all the above described three cases of variation of the contact surface with pressure, were observed.

Bikerman and Raydil studied the reversibility of friction forces during unloading. The tests were conducted on an inclined plane with square plates made from paraffin, tin, brass, glass, and chromium, weighing from 0.2 to 20 grams. The friction force was studied by the formula $f = W \sin \alpha$, where f is the force of friction, W is the weight of the load, and α is the angle of inclination of the plane at which sliding began. Determinations were made of the following: the friction force f_1 , requisite for the beginning of the sliding of the test plate under its weight; the friction force f_2 (after applying an additional load equal to the weight of the test plate); and the friction force f_3 , after the removal of the additional load.

Particular care was taken to avoid displacing the plate during the addition and removal of load. No attention was paid to the presence or absence of surface contaminations. Bikerman and Raydil established that, in the case of all the tested materials, with the exception of paraffin, within the range of errors of the experiment, $f_1 = f_3$. For the sliding of

paraffin on paraffin, $f_3 : f_1 = 1.45$, for the sliding of paraffin on tin $f_3 : f_1 = 1.30$ (i.e. a residual contact surface was formed). They concluded that the contact surface could not have been formed due to plastic deformation. In their opinion, the presence of plastic deformation presupposes $f_3 > f_1$, since no forces exist which could, during the removal of the load, break a plastically deformed contact.

The error committed by the above two observers is very characteristic. In reality, regardless of whether the application of the load induced elastic or plastic deformation, the removal of the load always releases internal elastic forces. These elastic forces, being absorbed after a finite time interval upon the removal of the load through the elastic after-effect, are specifically equal to the load being removed, and they tend to break the residual contacts. Frequently, as already indicated above, the elastic molecular forces may disrupt the contact completely, and, in such cases, the process of change in the magnitude of the contact surface, when applying and discontinuing the load, will seem to be reversible.

It would be, however, erroneous to conclude, on the basis of the seeming reversibility of the process, that the application of the load induces a reversible deformation. In this case, we simply could not register the non-reversible nature of the deformation. For instance, prior to the application of the load the test body was resting upon one contact protuberance, while the second protuberance was at a distance of 1,000 atomic layers from the bearing surface. Upon the appli-

cation and the removal of the load, the contact is again effected through the first protuberance, but the second one is now already at a distance of only 10 atomic layers from the surface. This is a non-reversible process, but it may appear as a reversible one.

10. The Toughness of the Contact

The resistance which must be overcome in order to disrupt the contact between solid bodies, in the absence of mechanical engagement, is determined by the product of the contact area (more precisely, the area of contact cross section) by the magnitude of the cohesion forces acting upon a unit of this area.

Examples of considerable cohesion between bodies, not preliminarily subjected to very high pressure, are few. Some information on this is available in the interesting theses by Jones^(27, 110). Macauley discovered a cohesion force of about 40 kilograms per square centimeter between the thin freshly foliated mica leaves. In this case, the adequate contact area was due to the ease of obtaining a smooth flat surface relief through the foliation of mica along the planes of cleavage, and also to the thinness and elasticity of the leaves, which promotes their snug fit. Tomlinson demonstrated the degree of cohesion of pure freshly sheared surfaces of lead.

Surface admixture films reduce considerably the strength of cohesion. Adsorbed gases have no direct effect upon the

7

toughness of the contact, as demonstrated by Holm's experiments, in which the cohesion between various metals (copper, silver, platinum, iron, nickel) was the same in a vacuum as well as in pure hydrogen and argon. Bowden and Hughes, in studying the coefficients of friction for copper, nickel, gold, and tungsten, thoroughly decontaminated from surface admixtures by vacuum-tempering, also obtained the same results in vacuum, hydrogen, and nitrogen. However, the admittance of even traces of air caused an immediate reduction in the coefficient of friction, due to the formation of oxidation films. The adsorption of water vapor, condensating at room temperature in liquid or solid state, sharply reduces cohesion. The admission into vacuum of gasoline vapors in the Holm and Kirchstein experiments⁽¹⁰²⁾, or the presence of mercury vapors in the Bowden and Hughes experiments, reduced cohesion and friction considerably.

The above cited examples, if not analyzed with great care, may lead to the erroneous conclusion that noticeable cohesion may be observed between pure surfaces only, and that surface admixtures, by themselves, will practically reduce cohesion between surfaces to zero. Such a viewpoint would be practically equivalent to an admission that there exist two classes of substances: pure, with considerable cohesion at contact, and impure, with cohesion at contact practically absent. Some authors do subscribe to this viewpoint. Thus, Jones takes pains in particularly emphasizing the purity of the metal and assumes that, granted an adequate degree of purity, the welding of metals may

be accomplished without heating and with the application of very low pressures.

Nevertheless, many examples of tough cohesion, in the presence of surface admixtures, may be cited. The difficulties of disassembling mechanisms and machinery that was standing idle over long periods, due to tough cohesion between the parts as a result of the formation of surface oxides (rust), is a matter of common knowledge. The dry lids of desiccators do not manifest any cohesion, while it is very hard to detach a vaseline-covered lid from the wetted and lubricated surfaces than to dry ones. A considerable cohesion between particles of oxides is very frequently observed. In yards of machine-building plants, the formation of solid lumps from oxidized metal chips can be observed. Methods for developing cohesion between metal particles by way of oxidation are utilized industrially. For sealing butt-joints in water pipes, packing with cast-iron chips, with the addition of small quantities of sulfur, ammonium chloride, and water, to induce the surface oxidation of the chip particles, is resorted to. Following oxidation, an exceptionally well set mass is formed, the cohesion between the particles of which and the pipe walls is so great that they are difficult to remove during repairs.

The same composition was used for the sealing of the butt-joints in the metropolitan subway tubings. Some methods of iron ore agglomeration are based on the addition and subsequent oxidation of iron or cast-iron dust particles.

It is, therefore, natural to pose the question as to why, in some cases, small surface admixtures of oxides and water vapors will disrupt the cohesion between two pieces of pure metal, while, in other cases, the formation of surface oxides, as a result of the effect of the air and moisture, will lead to the cohesion between pieces of metal, when laid up over a period of time.

The answer to this question was already given in part in paragraph 9 and other subdivisions of this book. As a result of rust formation during the periods of idling, the oxides fill the spaces between the contiguous iron surfaces. The thus formed contact surface is non-stressed or, at any rate, its internal stresses are considerably below the σ_k value. Therefore, the contact between such oxidized surfaces is distinguished by tough cohesion, for the disruption of which rather considerable external forces are required.

Not so is the case of a contact between two oxidized surfaces that was formed as a result of cold deformation under the effect of external pressure. Such a contact is a "stressed" contact, and, upon the removal of the pressure, no application of external forces will be required for its disruption, since it will be disrupted by internal stresses as a result of the elastic aftereffect in unloading.

The presence of surface admixtures facilitates the disruption of "stressed" contact for the following reasons:

(1). If the basic metal is harder than the admixtures (as in the case of oil films), the disruption is facilitated by the fact that the size of the contact surface is determined by the strength of the metal, and the tensile strength of the contact -- by the strength of the admixtures.

(2). If the admixtures are harder than the basic metal (as, for example, aluminum oxide), the disruption of the contact will be promoted by two factors:

(a) although the σ_R -value for the brittle oxide is greater than for the metal, its resistance to disruption is, on the contrary, less than for the metal;

(b) since the σ_R -value for the oxide, in this case, is greater than for the metal, the absolute size of the elastic deformation of the contact sections in unloading (paragraph 9, Table 9) will also be greater.

The effect of surface admixtures on the toughness of a "stressed" contact can be illustrated by examples.

Briquettes of the following materials were pressed under a pressure of 3,000 kilograms per square centimeter: (1) from iron powders; (2) from very fine soot-graphite; (3) from mixtures of iron powders with 2 percent graphite. The graphite was thoroughly intermixed with the iron powders in such a way that the iron particles were enveloped by the particles of graphite, and the contact between the iron particles was effected through a graphite film. The pure iron powder briquettes

and the pure graphite briquettes were of adequate toughness, while the iron-graphite mixture briquettes lacked toughness and showed cracks, due to the elastic aftereffect upon the removal of the pressure. This experiment revealed that the inadequate cohesion in the presence of surface admixtures is due not only to the low toughness of the contact (pure graphite and pure iron contacts had considerable toughness), but also to the differences in the value of the critical stress σ_R as between the graphite and the iron.

As another example, we will cite the commonly known seasonal fissuring of stressed brass. In this case, internal elongation tensions cause the fissuring of the metal as a result of the weakening of the bond between the brass crystallites following selective corrosion. This example indicates that the combination of the effect of internal stresses with the presence of admixtures may lead not only to the disruption of contact between metals, but also to the disintegration of the metal itself.

Experiments, which may help in the quantitative evaluation of contact toughness between pure metallic surfaces, are not numerous. As per the data gathered by Holm and his collaborators the cohesion between nickel contacts in vacuum, upon the removal of the load, amounted to 70 percent of the previously applied pressure, while in the air, cohesion amounted to zero. In a later thesis, Holm, while making computations on the basis of measuring the coefficient of friction and contact conduc-

tivity, discovered that the cohesion toughness of a nickel contact in vacuum is eight times greater than the temporary resistance to disruption. Holm explains this high value of cohesion toughness by the fact that the temporary resistance to disruption is always below the real toughness of the metal due to the presence of local structural defects.

It must be noted that temporary resistance to rupture, as related to the initial cross section area of the specimen, is not characteristic of the actual tensile stress at the breaking point, as related to the transverse section area at the moment of the break. Figure 13 shows the Stead diagram⁽¹⁴⁶⁾ of the actual tensions during the elongation of copper as related to the actual cross section of the specimen, with the reduction in the cross section area during the test taken into account.

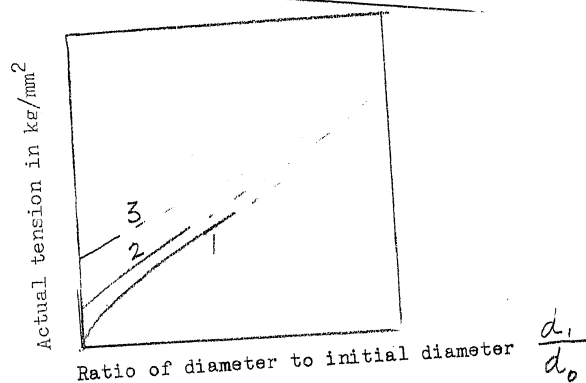


Figure 13. The diagram of actual tensions during the elongation of copper (as per Stead): (1) non-cold-hardened; (2) deformed to the extent of 23 percent; (3) deformed to the extent of 84 percent.

The following deductions may be drawn from this diagram:

(1). The actual tension at the moment of rupture for non-cold-hardened copper was 50 kilograms per square millimeter, which is $2\frac{1}{2}$ times greater than the temporary resistance and somewhat greater than the critical stress σ_R for non-cold-hardened copper. Such results are natural, since elongation was in excess of the cold-hardness.

(2). The actual tension at the moment of rupture was approximately the same for both the cold-hardened and non-cold-hardened specimens, which is natural, since deformation considerably toughens the non-cold-hardened copper and does not toughen the maximum cold-hardened copper.

(3). The diagram permits the extrapolation of the theoretical resistance of a material to rupture, which is to exist under conditions of reduced cross section areas down to zero. Such extrapolated values of tensile strength converge for cold-hardened and non-cold-hardened specimens at one point, and constitute about 90 kilograms per square millimeter, i.e., about $2\frac{1}{2}$ to 3 times greater than the critical stress σ_R and 4 to 5 times greater than the temporary resistance to rupture of non-cold-hardened copper.

According to O'Neil, such theoretically extrapolated tension value is three times greater than the σ_R value of non-cold-hardened and 4 to 7 times greater than the temporary resistance to rupture of the same.

It may be assumed with adequate plausibility that the strength of the contact between purely metallic surfaces is a magnitude of the same order as the strength of the metal itself.

Thus, in the case of pure metallic surfaces, the internal stresses, equal to the critical stress value σ_R , cannot induce the disruption of the contact, since the actual contact strength may exceed the σ_R value of the pure non-toughened metal. Hence, such a contact surface, upon the removal of the load, will retain its initial dimensions.

However, it is necessary to underscore that the residual surface will also be a stressed surface, it being the case that the magnitude of the contact stresses will equal the σ_R value.

In metallic surfaces with admixtures, as already indicated in paragraph 9, Table 9, the retaining of some part of the contact surface upon the removal of the load is more probable in the case of metals of lower hardness.

To the already indicated cause of this phenomenon (a lower elastic deformation value of the contact sections in the case of soft metals), let us add the following:

(1). To quote from Table 9, the elastic stress (equal to the σ_R value), tending to disrupt the contact, is 160 times greater in the case of tungsten than in the case of lead. Whereas, in all probability, the resistances to rupture of the surface films on tungsten and lead are much less apart. There-

fore, the elastic forces, released by the removal of the load, will more easily disrupt the contaminated tungsten contacts than those of lead.

(2). Under the same load, a lead surface is subject to a deformation 160 times greater than a tungsten surface. Therefore, in the case of lead, there is a greater drawing-off and displacement of surface admixtures, as a result of the extension of plastic deformation to a greater depth, the pressing out of the admixtures, and the advancing of new surface sections.

(3). Very soft metals, such as tin and lead, are at the same time easily-fusible metals, with a temperature of recrystallization and regression (repose) near room temperature. Hence, a diminution in the "strain" of the contact is possible at the expense of regression and recrystallization.

11. The Displacement of the Contact Surface in Sliding

The sliding of bodies in the direction of their plane of osculation (see Figure 8) is linked to a series of phenomena. In sliding, the previous contact sections are displaced and substituted by newly formed sections which, in turn, are displaced and substituted by others, etc.

To overcome interference in sliding, work is expended, the so-called work of friction. Part of this work is expended for the disruption of the cohesion between the contact sections of the surface. Another part of the work is used to overcome the engagement between the surface protuberances, for the

accomplishment of which the protuberances must be deformed. The deformation of the protuberances may be elastic, plastic, or brittle. The work of bearings furnishes a series of examples showing that in friction all these types of work occur. In the seizing of bearings, cohesion between the bearing bushing and the shaft occurs, as a result of which part of the bearing material is forced off and adheres to the shaft. As a result of plastic deformation, the surface of the bearing is run in to the shaft, while brittle and abrasive deformation result in the wearing out of the bearing and the shaft.

The work expended for the disruption of cohesion is in direct ratio to the size of contact surface (for brevity, we use in this paragraph the expression "contact surface" in place of "the projection of the contact surface upon the plane of sliding"). The work used to overcome the engagement between the irregularities of the surface through deformation, is also in direct ratio to the contact area (since it is specifically the irregularities, forming the contact, that are subject to deformation). Hence, the total work of friction, for the given path of displacement, is also in direct ratio to the contact surface:

$$W = k A_n l \quad (11/1)$$

where W is the work of friction,

A_n is the projection of the contact surface upon the plane of sliding,

l is the path of displacement,

k is the constant coefficient

This equation can also be presented as:

$$\frac{W}{l} = f = k A_n \quad (11/2)$$

where f is the force of friction, i.e., the force of friction is also in direct ratio to the contact surface.

The projection of the contact surface A_n , as per formula (6/2), is in direct ratio to load P :

$$A_n = \frac{P}{\sigma_R}$$

where σ_R is the critical stress.

Hence, the Amouton-Coulomb law on the direct ratio between the force of friction and the normal load:

$$f = \frac{k}{\sigma_R} P = \mu P \quad (11/3)$$

where μ is the constant coefficient of friction.

Footnote. This ratio, as analyzed by Bowden and Leben, and by Bowden and Tabor, is of a statistical [static?] nature. actually, the magnitude of the coefficient of friction, in sliding, oscillates at all times.

The work of friction is transformed into heat. In this process, the temperature of the surface layer, as demonstrated by Bowden and Ridler⁽⁸²⁾, may become very high, and, in the presence of considerable speeds of sliding, it may reach the melting point.

The magnitudes of the friction forces and the coefficients of friction depend greatly on the surface admixtures. In the experiments by Bowden and Hughes with pure metal surfaces of tungsten, nickel, copper, and gold, attained through vacuum-hardening (rarefaction of vacuum below 10^{-6} millimeters), the coefficients of friction were within the range of 4.5 to 6. The same metals, with surfaces contaminated by admixtures, showed a value of μ 0.3 to 0.6. Figure 14, as per Campbell, is a graphic illustration of the drop in the static coefficient of friction of copper against copper in relation to the thickness of the surface sulfide film:

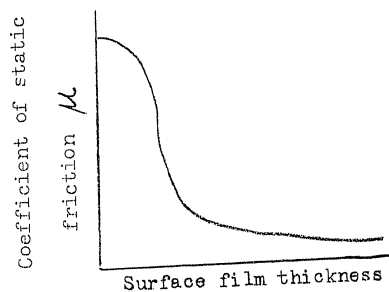


Figure 14. Ratio between coefficient of friction and surface film thickness (as per Campbell)

The question as to what part of the work and the friction forces is consumed for the disruption of cohesion and what part

is consumed for the deformation of the contact surface is of basic importance. It can also be formulated as follows: are the phenomena of friction, basically, a manifestation of mere surface cohesion, or are they also a manifestation of the volumetric (deformation of the deeper layers) properties of metal.

Hardy, Tomlinson, Holm, and others assume that friction is almost entirely determined by cohesion. Holm avers that the maximum work of friction is consumed for the overcoming of cohesion, and only 10 to 20 percent for the deformation of protuberances.

Bowden and his collaborators believe that not only the surface, but also the volumetric properties of the metal affect the phenomena of friction, since the size of the surface irregularities is great as compared with the size of molecules (see paragraph 3, Tables 2 and 3), which results in the extension of deformations to a rather considerable depth.

The author considers it probable that a considerable part of the work is consumed for the overcoming of the engagement between the protuberances. The Campbell analysis, for one, speaks in favor of this assumption (see Figure 14). The static coefficient of friction between pure copper surfaces had a magnitude of 1.14. In the presence of an unbroken film of sulfide admixtures with a thickness of $1,000 \text{ \AA}$ (i.e., on the order of several hundred atomic layers), the value of the coefficient

dropped to 1.0 only, and only in the presence of a film with a thickness of $2,800 \text{ \AA}$ (on the order of a 1000 atomic layers) it dropped to 0.78. If friction were determined predominantly by cohesion, the static coefficient of friction would always be the same, regardless of the admixture film thickness. Seemingly, during the oxidation of the surface protuberances to a greater depth, their toughness decreased, which facilitated deformation and reduced the coefficient of friction considerably. In the experiments of Bowden and Hughes, the kinetic coefficient of friction between nickel surfaces, thoroughly purified by vacuum-hardening, had a value of 4.5. Upon the admission of a small amount of oxygen and heating, which resulted in the formation of a visible oxidation film, the coefficient of friction was reduced to the value of 3.0, and, only after 24 hours of standing, it dropped to its normal value of 0.25. The drop in the value of the coefficient of friction from 3.0 to 0.25 can hardly be due to cohesion, since, in the presence of unbroken oxidation films in both cases, surface cohesion could not significantly differ.

This phenomenon is easier to explain by the decrease in the toughness of the surface protuberances as they are oxidized to greater depth.

A considerable diminution of the coefficient of friction, in the presence of thoroughly machined pure non-lubricated surfaces (by 60 percent and more as compared to poorly machined surfaces), may serve as an additional confirmation of the opinion

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A considerable diminution of the coefficient of friction, in the presence of thoroughly machined pure non-lubricated surfaces (by 60 percent and more as compared to poorly machined surfaces), may serve as an additional confirmation of the opinion

that the greater part of the work of friction is consumed not for the disruption of cohesion, but for the overcoming of the engagement between the surface protuberances.

CHAPTER III

METAL POWDERSBasic Data on the Structural Elements of Metal Powders

All free-flowing bodies consist of particles and interparticle (external) pores.

Powder particles, in turn, may be divided into finer structural elements. Metallic particles practically always contain admixtures, which are distributed both along the surface, as well as in the form of internal inclusions, and they frequently have intraparticle pores.

(1) Particles

Particles are structural individuals (bodies of minute dimensions), into which the substance of the powder is divided. As already pointed out in paragraph 1, the following is characteristic of particles.

(a) The individual isolation of the particles, i.e., their capacity for displacement and deformation to a greater or less degree independently of the neighboring particles.

(b) The presence of an incomplete mutual contact which is effected only on a small part of the particle surface, while the greater part of the surface is isolated from the contact by the interparticle pores.

(c) The "stressed" nature of the contact and the non-

permanence of the contact surface value. The size of the contact surface is a function of the pressure applied, it being the case that, at the places of contact, rather considerable stresses are concentrated.

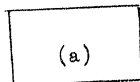
(d) The impurity of the metallic contact between the particles, the contact being effected through an interlayer of admixtures.

(e) The low strength of the bond between the particles which is due to the incomplete and stressed contact and also to the presence of admixtures.

Footnote. Some authors use the term "grain" or "crystallite" instead of "particle", which is not expedient, since the grains of a compact metal differ from the particles of powders by the nature of their mutual bond. In addition, particles, in some cases, are conglomerates of crystallites. The most appropriate term in this case would be "corpuscle".

Under the effect of cohesion forces, the particles are sometimes combined into rather sizable conglomerates, the dissociation of which requires a certain amount of work (see Figure 15).

Microphoto



Microphoto

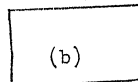


Figure 15. Reduced iron, magnified x 500: a. non-pressed;
b. briquette

The particles, in turn, may consist of smaller subdivisions, microscopic or submicroscopic. Thus, particles of powders obtained through the grinding of compact metals are subdivided into crystallites (Figure 16), the particles of carbonyl iron are subdivided into submicroscopic structural elements about 0.01 of a micron in size⁽¹³⁴⁾. Due to plastic deformation, a subdivision of the particles into sliding blocks is also possible. According to Smekal⁽¹⁴¹⁾, actual crystals are generally of a mosaic structure, being subdivided into finer elements of a submicroscopic order.

Microphoto

Figure 16. Ground cast-iron. Magnified x 500

A number of foreign authors (Schlecht, Schubard, and Duftschmid⁽¹³⁴⁾, Trzebiatowski⁽¹⁵¹⁾, and others) designate these subdivisions of the particles by a term borrowed from colloidal chemistry, "primary particle", and the particle proper as "secondary particle". This terminology is less expedient, since, on the one hand, it causes confusion in the concepts, and, on the other hand, the term "particle" is associated with a series of characteristics (incomplete, non-stable, and stressed contact, individual isolation), which are manifested very weakly in the subdivisions of a particle. By the nature of their internal bond, such structural subdivisions rather approximate the grains of compact metals than the particles of free-flowing bodies.

The particles may also have internal fissures, internal capillaries, pores (Figure 17), and admixtures -- surface and intraparticle.

Microphoto

Figure 17. Particles of electrolytic iron with internal pores.
Magnified x 250

The particles may be of a great variety of sizes and shapes. The form of the particles is determined by the method of preparation of the powder, and their shape -- by the technological cycle.

The size of the metal powder particles fluctuates within the range of 0.1 of a micron to several millimeters.

The form of the particles varies. The various structures can be divided into three basic groups:

(a). Fibrous or acicular particles, with a length considerably in excess of the other dimensions (Figure 18,a). Thin cast-iron chips are of acicular structure (Figure 19).

(b) Flat particles (platelets, leaflets, pads), in which the length and the width are many times in excess of the thickness (Figure 18,b). Such a structure is characteristic of metallic pigments.

(c). Equiaxial particles with all three dimensions approximately equal (Figure 18,c).

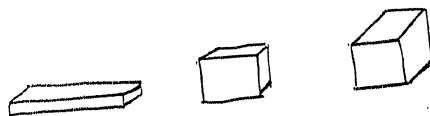


Figure 18. a. acicular; b. flat; c. equiaxial particles

Microphoto

Figure 19. Semi-steel chip. Magnified x 100

There are many varieties of the above basic groups (for instance, equiaxial particles may be spherical and polyhedral), and also intermediate forms in between, as for instance, electrolytically obtained dendritic structures, in some cases, approximate acicular (see Figure 20), in other cases, equiaxial or flat in shape.

Microphoto

Figure 20. Electrolytic copper. Magnified x 150

Similarly to continuous bodies, particles have numerous protuberances and concavities. There are smoother and rougher particles.

There is also the concept "surface porosity" of small particles. Let a spherical particle with a diameter of one micron (Figure 21) have protuberances 0.15 of a micron in height, it being the case that $1/3$ of the volume of the spherical

surface zone, having a thickness of 0.15 of a micron, is taken up by these protuberances, while $\frac{2}{3}$ of this zone is not occupied by the metal. It is not difficult to compute that, in this case, 43 percent of the entire volume of the particle will fall to "surface porosity". The presence of some "surface porosity" is shown by the microphoto of a particle of metal powder, as prepared by Ardenn, under an electronic microscope (Figure 22).

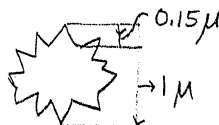


Figure 21. Diagram of "surface porosity"

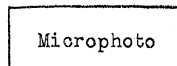


Figure 22. Metal powder particle as seen under an electronic microscope (by Ardenn)

(2) Pores

The particles are separated from one another by pores (interparticle) and contact intervals. By pores we designate the voids, through which no mechanical stresses can be transmitted, i.e., their diameter is greater than the effective radius of the molecular forces. The transverse dimensions of the contact intervals, which separate the surface contact sections are not in excess of the effective radius of the cohesion forces.

In non-compressed metal powders, the pores occupy over 50 percent of the entire volume, usually 70 to 85 percent. In

some cases, 98 percent of the entire powder volume is occupied by the pores. Figure 23 is a visual illustration of the great extent of the space occupied by the pores and of the small number of contacts between the particles. It must, however, be taken into account that the microphoto shows a transverse section of the slide, and that the number of contacts in depth is much greater.

Microphoto

Figure 23. Copper powder obtained by the reduction of water solutions of copper sulfate. Magnified x 250

In addition to interparticle pores, the powders may have intraparticle pores (see Figure 17).

By their absolute magnitude, pores are classified as macroscopic, microscopic, and submicroscopic. The size of interparticle pores increases with the increase in the size of the particles and a diminution in the density of their stacking-up pattern. Alongside of the interparticle pores, the size of which is of the order of magnitude of the powder particles, large voids occur of a size many times greater than the size of the particles. Meldau and Stach⁽¹²⁴⁾, in experimenting with lead shot, observed large voids stipulated by a sort of "arch effect", a formation of overlap between the particles. An indirect indication of the size of individual pores is their permeability to gases and liquids -- the greater the permeability, the larger the pores.

(137)
 Seelheim experimented with the amount of water running through a layer of sand 40 centimeters thick during a 15 minute time interval under a pressure of 50 centimeters. The results of these experiments for various groups of sands, with particle radii from 81 to 336 microns, are presented in Table 10. The conclusion was drawn that permeability runs in direct ratio to the square of the particle diameter (or, which is the same, to the square of the pore diameter).

TABLE 10

Permeability of Sands of Various Particle Size, as
per Seelheim

Particle radius	Volume of water running through in 15 minutes (in cm ³)	Ratio between square
		of particle radius and volume of water
336	130.9	625
238	89.7	621
113	21.02	610
81	10.3	636

On the basis of measuring their accessibility to liquids not reacting with the powders (determinations are usually made for oil), the pores are classified into open ones (communicating, capillary) and closed ones (isolated).

Footnote: Instead of open and closed, it would be more specific to classify the pores into accessible and non-accessible to a given liquid under predetermined conditions. The experiments by Tammann, for instance, revealed that, under high pressures, the pores of compact metals, seemingly insulated, may be impregnated with liquids. Figure 23 above is a visual illustration that in non-compressed metal powders all interparticle pores are communicating pores. The intraparticle pores may be both open as well as isolated.

(3) Admixtures

Due to the small size of their particles, surface phenomena in powders play a considerably greater part than in compact bodies.

If a cube with a rib of magnitude a and a surface $6a^2$ is subdivided into n^3 cubelets with a rib magnitude of $\frac{a}{n}$, the total surface of the smaller cubes formed will equal $n^3 \times \frac{6a^2}{n^2} = 6na^2$. This example shows that the specific surface (or the surface of a unit of mass, in some cases, of a unit of volume) is in inverse ratio to the diameter of the particles. Table 11, first compiled by V. Ostwald, cites the dimensions of a surface of 1 cm³ of a compact substance subdivided into cubelets with various rib magnitudes.

TABLE 11

Surface Magnitudes of 1 Cubic Centimeter of Compact Substance in
Relation to the Degree of its Subdivision (as per V. Ostwald)

The length of the Cube- let rib	The sur- face (in cm^2)	The length of the cubelet rib (in microns)	The surface in μ^2
1 cm	6	1	6
1 mm	60	0.1	60
0.1 mm	600	0.01	600
0.01 mm	6000	0.001	6000

The microscopic determinations of the particle magnitudes, as well as the geometrical mensurations of compact body surfaces, do not give the true concept on the size of the specific surface, due to the presence of microscopic and submicroscopic irregularities, concavities, protuberances, capillaries, and fissures. In powders, the specific surface, computed by adsorption of pigments, is hundreds and even thousands of times greater than the apparent geometrical surface computed on the basis of microscopic measurements of the size of particles⁽⁴⁰⁾.

Due to the considerable size of the specific surface, the amount of surface admixtures per unit of mass (mainly oxides) in powders, particularly in fine ones, is considerably greater than in compact bodies. The absolute thickness of the surface admixture films on the powder particles is just as insignificant as in the case of compact bodies, yet, due to the smallness of the particles, the volume of the admixtures constitutes a

rather appreciable part of the metal volume.

Footnote. The thickness of the surface films (usually of the order of a hundred or several hundred atomic layers) can be with equal logic designated both significant and insignificant. It is insignificant when measured in the macroscopic or even in the microscopic scale, but becomes rather significant when measured in the atomic scale.

Some specifications for the delivery of powders anticipate the permissibility of oxygen content up to 0.5 -- 1 percent. If we assume that the oxygen is in a chemically combined state, then, for example, in the case of copper powders, 0.5 to 1 percent of oxygen will correspond to 4.5 to 9 gravimetric percentage of cuprous oxide (Cu_2O). Oxides have a lower specific gravity than metals, hence, the volumetric share of the admixtures is still more considerable. The admixture layer is not always uniform throughout its entire depth, since the surface layers may be to a greater or lesser degree enriched with oxide inclusions, the degree of concentration of which is gradually diminished in the direction from the periphery to the center of the particle. This phenomenon will sometimes even enlarge the "effective sphere" of the admixtures.

Therefore, the deformation of powders, in a number of cases, will differ from the deformation of compact bodies. Figure 24 shows that, assuming the same relative deformation, large bodies will manifest the deformation of the basic metal predominantly, while small particles will manifest the deformation of the admixture layer predominantly.

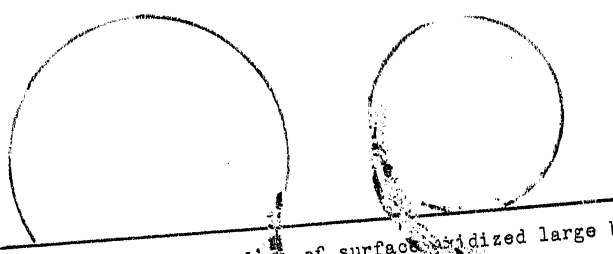


Figure 24. Deformation diagram of surface oxidized large body and small particle

In addition to oxides, the surface layers are enriched with gases and vapors, a part of which is in a state of adsorption, while the greatest part adjoins the adsorbed monomolecular layer. It is possible that the layer of vapor on the particle surfaces is condensed into water. According to the evaluation by Trzebiatowski⁽¹⁵¹⁾, the amount of adsorbed gases may have a magnitude of the order of several cubic centimeters per one gram of powder. According to Stromberg, a gold surface, subjected to an atmosphere of water vapors for several hours, becomes covered with a film 0.006 of a micron thick (i.e., of the order of ten molecular layers). It must be remembered that surface oxides (in contradistinction from gold) usually are hydrophilic, and are capable of absorbing considerable quantities of water, it being the case that such oxides become plastic, soft, and easily amenable to deformation.

Footnote. In colloidal chemistry, colloids reacting with water, such as clay and numerous oxides, are called hydrophilic, in contradistinction to colloids not reacting with water, such as gold and other metals, which are called hydrophobic.

Powders also contain intraparticle admixtures -- inclusions of contaminations, oxides, and the like. In powders obtained through reduction, the oxides are located predominantly in the central zone of the particle (see Figure 25) into which zone no adequate amount of the reducing agent was diffused.

A mechanical contamination of powders by individual admixture particles is also possible.

Admixtures entering into solid solution or chemically combined admixtures are also present in powders, usually in the same amounts as in solid metals

Microphoto

Figure 25. Incompletely reduced oxides (dark) inside the iron particles obtained through reduction from slag. Magnified x 250

A powder particle is as a world in miniature. (Figure 26). Like the Earth, the metal particles are surrounded by an atmosphere, and on their surfaces takes place the condensation of relatively large amounts of water vapors. The terrestrial surface is covered with countless fragments of rock formations, sand, stones, and the like. The powder particles, too, are covered with fragments of brittle oxides. The protuberances and concavities of the particle surfaces correspond to the mountains, hills, and synclines of the terrestrial configuration. The hardness of the particle surface oxides, under

various degrees of humidity, fluctuates in the same manner as does the hardness of terrestrial clay. The dry oxides are hard and brittle, like stone or dry clay, while the damp ones are soft and plastic like dough or wet clay. It is also to be remembered that the state of the powder particle surface is subject to continuous change, as is the state of the terrestrial surface (only the changes are more rapid).

13. The State of Free-Flowing Bodies Under the Effect of Their Own Weight

Up to here we were analyzing the individual structural elements of metal powders. Now we will proceed with the analysis of powders as an aggregate of very great numbers of particles, the sizes of which are very minute as compared to the volume of the entire conglomerate. It has been computed that the number of particles in 1 cubic centimeter of the industrial grade of tungsten, molybdenum, or tungsten carbide powder reaches into several billions, i.e., greatly in excess of the population of the entire world.

Although each separate particle of a powder is an individual in itself, the processes taking place in a conglomerate consisting of millions or billions of such individual corpuscles are of a "statistical" nature. The aggregate of great numbers of particles in mutual contact is known as a free-flowing body.

Some analogy can be drawn between liquids and free-flowing bodies; under the effect of their own weight, like liquids,

assume the shape of the container in which they happen to be. It must, however, be remembered that the number of differences between the above two classes of substances is greatly in excess of the number of similarities. The basic differences are as follows below.

(1). The "fluidity" of powders is much below the fluidity of liquids. Powders do not fill all possible convolutions of a complex mold to as complete an extent and as rapidly as do liquids.

In the pressing of powders, no parts of such complex shapes as are obtainable in the pressing of plastic masses or in casting under pressure, are attainable. The lower fluidity is due to the considerable internal friction of free-flowing bodies.

(2). Freely poured powders, in contradistinction to liquids, do not spread indefinitely, but form a conical pile (Figure 27).

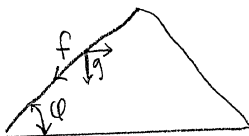


Figure 27. Forces active in a powder pile

The angle of the pile slope to the horizon (φ), the so-called angle of natural repose, for most of the free-flowing bodies fluctuates within the range of 25 to 70 degrees. Let us dissociate the weight of a powder particle into two components, one normal to the plane $N = g \cos \varphi$, and one in the direction of the plane $f = g \sin \varphi$, the $f = N \tan \varphi$. For the equilibrium of the particle, it is necessary that the force of friction, which is counteracting the displacement,

equals f . The force of friction is in direct ratio to normal pressure N so that $f = \mu N = N \tan \varphi$. Hence, the coefficient of friction μ equals the tangent of the angle of natural repose φ , i.e., the angle of natural repose φ is the friction angle.

(3). The pressure in a free liquid, in conformity with Pascal's law, is transmitted equally in all directions. In contradistinction to this, in free-flowing bodies, the specific pressure in the direction normal to the line of its application has a magnitude of approximately 20 to 30 percent of the applied specific pressure. Pressure is not distributed uniformly, and, within the limits of individual powder particles, it is localized predominantly in the contact sections of the particles.

(4). A liquid will fill completely and without inter-spaces the volume of the container. In contradistinction, the particles of a powder, under the effect of their own weight, will occupy the smaller part (about 15 to 30 percent) of the volume of the container into which they are poured.

(5). The volumetric deformations of a liquid in a container are elastic and reversible. The deformations of free-flowing bodies are to a considerable degree non-reversible.

(6). Liquids are isotropic. In contradistinction, the particles of free-flowing bodies are usually orientated

(are disposed with the greatest cross section normal to the force of gravity). Hence, the properties of free-flowing bodies, such as porosity, gas-permeability, electric conductivity, are not the same in different directions.

A characteristic of free-flowing bodies is the non-stability of the magnitude of the contact surface between the particles, which is a function of the external stresses. The strength of free-flowing bodies, in its turn, is a function of the contact surface, and, hence, in the final analysis, a function of the applied external stresses. The strength of free-flowing bodies, as we will see further down in the text, is usually some fraction of the stress applied during the formation of the body. Since the forming pressure in the case contemplated here equals the weight of the free-flowing body, the resistance of free-flowing bodies to tensile break is insignificant (many times less than its own weight). Nevertheless, free-flowing bodies always have some ultimate tensile strength value (see Chapter VII).

The volumetric characteristics of some powders are given in Table 12, from which it can be seen that the part of the container volume filled with the particles of a freely poured powder fluctuated within the range of 3.8 to 52 percent, while the same value in the case of a shaken down powder fluctuated within the range of 12.9 to 67 percent. The increase in the density as a result of the shakedown oscillated from 1.1 times, for powders of maximum density to 3.1 times, for the most friable powders.

TABLE 12

Volumetric Characteristics of Some Powders

No. in sequence	Powder	Pouring weight in grams/cm ³	Shaken down weight in grams/cm ³	Relative density of poured powder (in %)	Relative density of shaken down powder (in %)	Ratio between shaken down weight and free ly poured weight
1	Iron oxide, fine	0.44	1.16	8.6	22.4	2.64
2	Iron, reduced from fine oxide at low temperature	0.30	1.02	3.8	12.9	3.40
3	Same, at high temperature	0.70	2.22	8.9	28.0	3.17
4	Iron, reduced from slag	1.97	3.12	25.0	39.6	1.59
5	Iron, electrolytic	2.70	4.34	34.3	55.8	1.61
6	Aluminum powder	0.27	0.71	10.0	26.3	2.63
7	Copper electrolytic	1.65	2.85	18.5	31.9	1.72
8	Copper electrolytic highly-oxidized	2.42	2.66	27.1	29.8	1.10
9	Copper, ball-mill, granulated	4.66	6.06	52.2	67.2	1.30
10	Tungsten reduced	1.93	5.12	9.7	25.6	2.65
11	Same as above	2.49	6.24	12.5	31.2	2.50
12	Tungsten, pouring weight 2.42, after pressing & grinding	4.53	9.52	22.7	45.6	2.10
13	Tungsten, reduced	4.91	7.40	24.6	37.0	1.50

The volume occupied by metal powders is always much greater than the volume corresponding to the maximum packing density of the powder particles. Thus, in the experiments conducted by the author with a spherical particle granulated copper powder, a porosity of 25 percent, corresponding to the maximum packing density, was attained only under a pressure of 4000 kilograms per square centimeter^(2,10). The next example shows that the pouring weight of free-flowing bodies is not determined entirely by their packing density. The densest packing of uniform spherical pieces is attained at a porosity of 25 percent, and of uniform cylindrical pieces -- at a porosity of 10 percent. Nevertheless, clippings of wire stack up to a lower degree of density than scrap shot or scrap pellets.

The well known colloidal specialist Gan⁽²⁴⁾ explains the friability in the packing of powders by the presence of surface films of light-weight admixtures. The next example the inconsistency of this explanation. From Gan's viewpoint, it should be expected that the oxidation of powders in storage is always to result in a diminution of its pouring weight, since the specific gravity of oxides is approximately $1\frac{1}{2}$ times lower than that of the corresponding metals. In reality, the opposite is true, i.e., the pouring weight of a powder is invariably increased with low-temperature oxidation, and invariably diminished with low-temperature reduction (See Table 13).

TABLE 13

The Effect of Oxidation on the Pouring Weight of ElectrolyticCopper Powder

No. in sequence	Powder	Oxygen content (in %)	Pouring weight in grams/cm ³
1	Electrolytic freshly ob- tained powder	0.09	1.25
2	Same as above, after 10 days storage in open air	0.56	1.34
3	Same as above, after a month in the open	1.8	1.49
4.	Same as above, after reduction at 500°C in a hy- drogen atmosphere	0.02	1.12

In the opinion of the author of this book, the magni-
tude of the volumetric characteristic of a powder is primarily
determined by toughness factors. When structures designed for
the same load and made of grades of steel of various strength,
but of the same specific gravity, have different weights, any

7

engineer will conclude that the lighter structure is made from the tougher material. The same conclusion is to be made with relation to powders.

A free-flowing body occupies a volume, at which its mechanical toughness, stipulated by the engagement and the interlocking of its particles, is adequate for the resistance to the load produced by the weight of its particles.

Footnote. This specifically is the mechanical toughness determined by the engagement and the interlocking, and not by the cohesion of particles. Toughness stipulated by cohesion is the same at any volume of the free-flowing body, since the size of the contact surface of the particles depends not on the volume of the free-flowing body, but only on the pressure applied. Engagement, on the contrary, increases rapidly with density.

If the "structural" toughness of a powder is great, an adequate number of engagements is assured even with loose packing, and the powder has a low pouring weight. If, however, the toughness of the "skeleton" of the free-flowing body is inadequate, it takes a greater packing density to attain the requisite particle engagements, and the powder has greater pouring weight.

The diagram below (see Figure 28) elucidates upon the above considerations.

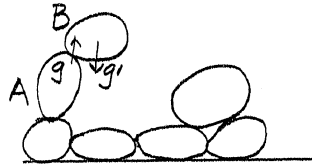


Figure 28. Diagram explaining the packing density of powder particles.

In pouring the powder, particles B fall on particles A. The pair of forces $G - G'$ ($G = G' = \text{weight of particle}$) tends to throw particle B downward. If the moment of this pair of forces is adequate to disrupt the engagement between particles A and B, particles will roll down, and the packing will be dense; otherwise, the particles will remain in the same position, and the packing will be loose.

Packing density depends on a number of different factors. These factors usually change the toughness of the powder, and the toughness of a free-flowing body determines its volumetric characteristic.

The most important of these factors are enumerated below.

(1). Size of the particles. The size factor greatly affects the packing density. When the particle diameter is increased tenfold, its weight is increased $10^3 = 1000$ times, and the tilting moment (see Figure 28) is increased $10^4 = 10,000$ times, whereas the absolute size of the irregularities and protuberances practically remains the same. Therefore, structural toughness is frequently lower, and pouring weight greater in powders with large particles as compared to finer powders.

CONTRACT INFORMATION

Additionally, in the case of powder with a higher dispersion, the pouring weight is decreased by the effect of "surface porosity". Table 14 cites the "surface porosity" of powders in which the height of the surface protuberances is 0.15 of a micron, with the protuberances occupying 1/3 of the entire surface zone (when the powder particles are of spherical shape).

TABLE 14

"Surface Porosity" of Powder Particles of Various Sizes with the
Height of Surface Protuberances Being 0.15 of a Micron

Diameter of particles (in μ)	Surface porosity (in %)	Diameter of particles (in μ)	Surface porosity (in %)
1	43	5	11
2	27	10	6
3	18	20	3
4	14	50	1

The pouring weight of quartz sand of various particle sizes (from 10 down to 2 millimeters) is indicated in Table 15 (as per Volni⁽²⁴⁾). It can be seen that the pouring weight increases with the diminution in dispersion.

TABLE 15

The Pouring Weight of Quartz Sand (as per Volni)

Volume of container (in liters)	Particle Size							A mixture of all fractions (from 10 microns to 2 millimeters)
	10-71 μ	71-114 μ	114-171 μ	171-250 μ	0.25-0.5 mm	0.5-1 mm	1 - 2 mm	
5	1.4162	1.4417	1.5610	1.6024	1.6444	1.6639	1.6914	1.8216
0.25	1.4009	1.4163	1.4652	1.5464	1.5688	1.6168	1.6339	1.7722

It must, however, be borne in mind that, in powders of various origin and various particle shapes, the diminution of pouring weight with dispersion may not occur.

(2). Shape of the particles. The fibrous and dendritic forms assure the maximum interlocking and engagement of the particles. Hence, such powders are the toughest and the lightest (in weight). Inversely, powders with equiaxial, particularly spherical particles, are the heaviest. Usually, the presence of particle conglomerations lowers the pouring weight of a powder.

The greater the particle surface roughness, the tougher and the lighter the powder.

(3). Distribution of particles by size. In the presence of a mixture of fine and coarse particles, the first may

dispose themselves in the spaces between the second, thereby increasing the packing density. As seen from Table 15 above, the mixture of all fractions of sand, with the particle sizes running from 10 microns to 2 millimeters, has the maximum pouring weight (as compared to the pouring weight of any separate fraction).

(4). Intraparticle porosity. The internal pores increase the volume of the particles without lowering the structural toughness of the powder, which is stipulated by the toughness of the surface, and not the internal, layers of the particles. Hence, powders with intraparticle porosity have a lower pouring weight than powders with compact particles.

(5). Surface Oxides. Oxides are more brittle than the basic metal. Therefore, the formation of oxides always results in lower toughness and higher pouring weight (regardless of the lower specific gravity of the material).

In some cases, the layer of surface oxides, in reacting with atmosphere moisture, becomes soft and acquires a dough-like consistency. This will also promote an increase in pouring weight.

(6). The treatment of powders. Ball mill grinding, in most cases, increases the pouring weight of powders (particularly the powders of plastic metals). The grinding of malleable metals is accompanied by the smoothening of the surface protuberances, the attenuation of the surface layer of oxides, the decrease in intraparticle porosity, which renders

the powders heavier.

In the grinding of powders of brittle metals, some of the factors increase the pouring weight of the powder (attenuation of the surface layer, improved packing density due to the formation of mixture of fine and coarse particles), while some other ones result in a diminution of the pouring weight (reduction in size of particles). Hence, grinding in ball mills may either reduce or increase (as in most cases) the pouring weight of powders.

Table 16 gives some data relating to the effect of the ball mill grinding period on the pouring weight of a reduced iron powder.

TABLE 16

The Effect of Grinding Time upon the Pouring Weight of a
Reduced Iron Powder

<u>Grinding time</u>	<u>Pouring weight</u>
<u>(in hours)</u>	<u>(in grams/cm³)</u>
Prior to grinding	1.26
1	1.40
2	1.46
3	1.52
6	1.63
12	1.75
24	1.94

(7). The effect of test conditions. The magnitude of the pouring weight is usually increased with the increase in the volume of the container (see Table 15) and with the height of the drop of the powder layer.

14. Various Methods of Expressing the Volumetric Characteristic of Porous Bodies

The volumetric characteristic of porous bodies may be expressed by one of the following magnitudes.

(1) Volumetric weight γ -- the weight of a unit of the body volume, expressed in grams per cubic centimeter.

In the case of powders, two weights are differentiated: the pouring weight (the weight of a unit of volume of freely poured out powder) and the shake-down weight (the weight of a unit of volume of a shaken down powder).

(2) Gravimetric volume ω -- the volume of a unit of weight of a porous body, expressed in cubic centimeters per gram:

$$\omega = \frac{1}{\gamma} \quad (14/1)$$

(3) Relative density ρ -- the ratio of the density of the powder to the density of the material from which the powder stems:

$$\rho = \frac{\gamma}{d} \quad (14/2)$$

where d is the density of the material of the powder.

The relative density is characteristic of a part of space occupied by the material (the "skeleton") of the powder, and is expressed by an abstract number, a regular fraction, or in percent ($\vartheta < 1$, or $\vartheta < 100\%$).

(4) Relative volume β -- an abstract number indicating the number of times by which the volume of the free-flowing body is greater than the volume of the initial material. It is expressed by an irregular fraction, or in percent ($\beta > 1$, or $\beta > 100\%$):

$$\beta = \frac{1}{\vartheta} \quad (14/3)$$

(5) Porosity π characterizes the part of the volume that is occupied by the pores, usually expressed in percent

$$(\pi < 100\%): \quad \pi = 1 - \vartheta$$

or

$$\pi = 100\% - \vartheta$$

(14/4)

(6) Coefficient of porosity ε -- an abstract number indicating the ratio of the volume of the pores to the total volume of the free-flowing body. It is expressed by an abstract number, or in percent, and it may assume any value from zero to ∞ :

$$\varepsilon = \beta - 1$$

or

$$\varepsilon = \beta - 100\% \quad (14/5)$$

The ratio between the coefficient of porosity and porosity is expressed by formulas:

$$\eta = \frac{\varepsilon}{\beta} \quad (14/6)$$

and

$$\varepsilon = \frac{\eta}{\eta} = \beta \eta \quad (14/7)$$

Together with the volume, the magnitude of all other characteristics of the porous body undergoes a change. The necessity frequently arises for the use of the so-called "reduced" magnitudes, i.e., magnitudes corresponding to a compact body of the same mass as the porous body.

Let us cite a few examples. The "reduced" volume of a free-flowing body V_R is the volume of the compact material (the "skeleton") of the powder.

$$V_R = V \eta, \quad (14/9)$$

where V is the volume of the porous body,
 η is its relative density.

The "reduced" height h_R of a powder press-mold charge is the height of a briquette, with the same cross section compressed to a compact state:

$$h_R = h\varrho,$$

(14/9)

where h is the height of the porous body,
 ϱ is its relative density.

The "reduced" specific work of compression is the work it takes to compress a quantity of powder corresponding to 1 cubic centimeter of compact material.

CHAPTER IV

COLD - DEFORMATION OF METAL POWDERS

15. General Notes

Deformation in a compact body in conformity with the literal meaning of this word, is a change of its form. Volumetric changes during the deformation in a compact metal are so insignificant that they can usually be disregarded. Deformation in a free-flowing body changes not only its form, but also its volume. In pressing, the volume is usually reduced 3 to 4 times at the expense of the diminution in porosity.

The deformation of compact bodies is easiest to observe in monocrystals. The phenomena of deformation in compact polycrystalline metals are more complex. Still more complex is the deformation of free-flowing bodies. During the deformation of a compact polycrystal, the outlines of each crystallite reproduces fully the changes in the boundaries of the adjacent grain, with more or less precision, also reproduces the change in the form of the entire body. For example, in compressing an ingot to half its size, the corresponding cross section of the grain is also reduced to half size. During the compression of powders, the particles may, to a certain degree, sustain deformation as individual bodies, and the outline of each particle must not exactly reproduce the outline of its neighbors. A free-flowing body undergoes changes not only at the expense of the deformation of the particles proper, but

also due to the displacement of the latter and the change in the volume of the pores. Hence, in compressing a briquette to half its size, the corresponding cross section of the particles may remain almost the same.

Figure 29 shows various types of deformation and displacement of particles taking place during the deformation of a metal powder.

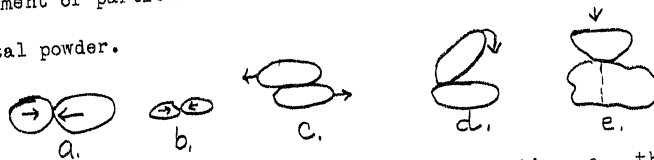


Figure 29. Displacement of particles in deformation: a. the converging of particles; b. the diverging of particles; c. the sliding of particles; d. the rotation of particles; e. displacement with subdivision.

(a) The converging of particles (Figure 29,a), leading to an increase in contact sections (in the first stage of drawing close there may be no contact yet between the particles).

(b) The diverging of particles (Figure 29,b), leading to a decrease in contact sections (the diverging of particles may end by disruption of contact).

(c) The sliding of particles accompanied by a displacement of contact sections (Figure 29,c).

(d) Rotation of particles (Figure 29,d).

(e) Displacement of particles linked with their subdivision as a result of brittle and abrasive deformation (Figure 29,e).

The displacement of the conglomerate particles, as analyzed statistically, and also the displacement of an individual particle, may simultaneously occur in several types of deformation. For instance, a particle may be displaced, with reference to one particle, according to type a, and with reference to another particle, according to type b.

In pressing, powders may sustain simultaneously elastic, brittle, and plastic deformation of their particles.

The contact phenomena in powders are also more complex. In the case of solid bodies, the contact surface may, in a number of cases, be considered as situated in one plane. In the case of free-flowing bodies, the contact sections of the particles are situated in many layers and in all directions to the pressure applied. In compact bodies, we could analyze separately the change in the size of the contact surface under the effect of normal forces, and its displacement under the effect of tangential forces. In pressing free-flowing bodies, some contact sections are subject to the effect of normal forces, other contact sections, to the effect of tangential forces, still other sections, to the effect of both normal and tangential forces. Hence, the change in the size of the contact surface cannot be analyzed separately from its displacement. The concept of a contact surface in free-flowing bodies is of a statistical nature.

Finally, even simple and conventional concepts, such as

stress and cross section, when applied to free-flowing bodies, become complex. In compact metals, stress is determined by the ratio of deformation force P to the area of the intersection of the specimen by a plane normal to the direction of the force (see Figure 30,a). In the case of powders, stress cannot be determined by dividing the deformation force P by the entire area of the transverse section of the free-flowing body, since stress is not transmitted through the pores. Obviously, the force is to be related only to the part of the transverse section which is not occupied by the pores. But it is not difficult to see that these parts of the area are by far not the same for a number of parallel intersections of the free-flowing body. For instance, in the intersection by plane 1-1, the stresses are transmitted through its entire area, while in the intersection by plane 2-2, the stresses are transmitted only through a small area of the intersection (see Figure 30,b).



Figure 30. Intersections normal to the acting force: a. in compact metal; b. in powdered metal.

Hence, the processes of deformation of free-flowing bodies may, at the first glance, seem exceptionally complex. Nevertheless, many phenomena occurring during the deformation of powders are, on the contrary, more simple than in compact bodies.

All the properties of compact bodies are related in a

complex manner to both the properties of the crystallites, into which they are divided, as well as to the characteristics of the bond between the crystallites. For instance, a fracture as a result of the deformation in a compact metal may be either intracrystalline or intercrystalline, depending on which of the two is the greater strength. In powder briquettes, the contact surface is so insignificant that the strength of the conglomerate is always determined, not by the strength of the particles, but by the strength of the bond between them, and fractures, when occurring, will run not through the particles, but between them.

(Footnote. The strength of compressed briquettes is frequently tens and hundreds of times below the strength of the corresponding compact metals). Subsequently, we will see that not only strength, but also other properties of briquettes, such as electrical conductivity, hardness, are "contact" properties, and they run in very simple relation to the size of the contact surface.

Footnote. This is not to be understood in the sense that properties of powders do not depend on the material of the particles, but only on the contact between them. As we will see subsequently, the properties of the material of the particles stipulate not the nature per se of the ratio between the degree of contact and the properties, but the magnitude of the numerical coefficients in these ratios.

Contact phenomena in compact bodies seem to be more simple than in free-flowing bodies until such time only as we deal with the external contact between various bodies. When passing on to the internal contact between the grains of a compact body, these phenomena become more complex. In the case of powders (compressed as well as non-compressed), all the sections of the internal contact surface (i.e., the surface of contact between the particles) are "stressed". It being the case that the stresses per unit of area of the projection of the contact upon a plane normal to the pressure are the same in each section, and they equal σ_K , the critical stress, at which non-reversible deformation begins. In a compact body, the intergranular contact is effected along the entire (or almost the entire) surface of the grains. During deformation of a compact body, the internal contact surface passes from a non-stressed to a "stressed" state, it being the case that the stresses, at various sections are not the same, and may be both equal to the σ_K -value as well as below the same. The contact surface of the particles of free-flowing bodies, as will be seen further down in the text, increases with pressure, with a simple quantitative ratio between pressure and the size of the contact surface. The contact surface of the grains in compact bodies, as shown by electrical conductivity determinations, on the contrary, decreases with deformation, it being the case that it is difficult to establish a definite quantitative ratio between the size of the contact surface and

the degree of deformation.

In order to introduce clarity into the study of deformation in free-flowing bodies, it is necessary to specify more accurately the concepts "stress" and "cross section" as applied to powder metals (see paragraph 16).

16. Maximum Stresses and Minimum Cross Sections in Powder Bodies.

Ratio between Contact Surface and Pressure

It is simple to realize that in the compression or in the elongation of a compact metal (see paragraph 15, Figure 30,a), the intersection by a plane normal to the acting force has the minimum area as compared to all other cross sections. Inversely, the elongation or compression stress in this intersection has its maximum value.

In a compact metal specimen (see Figure 30,a), any intersection by a plane normal to the acting force has the same and the minimum area value.

In contradistinction to this, in the case of powder metal, various intersections by planes normal to the pressure have a different and usually not the minimum area, occupied by the metal (but not by the pores). We are primarily interested in intersections with minimum metal surface values. These, being the most attenuated spots, with the maximum concentration of stresses, determine the toughness and the behavior of the powder metal in deformation. As a rule, the intersection of the powder metal by a plane normal to pressure, will not be the

most attenuated, since it runs not only between the particles, but also through them. The most attenuated intersection with minimum area is the intersection by a broken surface which passes exclusively through the pores and through the sections of mutual contact.

Let us have in a press mold a rectangular powder briquette under pressure P , and let HH be its intersection by a horizontal plane (see Figure 31). Plane HH intersects one layer of particles. The surface of the contact of this "solitary" layer of particles with the next horizontal solitary layer in Figure 31 is indicated by heavy lines (It must be remembered that the "solitary" layer is rather a mathematical than a physical concept).

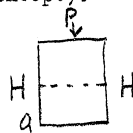


Figure 31. Contact surface of "solitary" layer

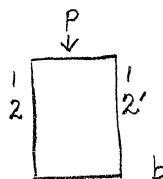


Figure 32. Contact section:
horizontal dot-and-dash line
 $H - H$ indicates the transverse,
the broken dot-and-dash line
indicates the contact section;
the dotted parts of the broken
line pass through the pores,
the solid parts pass through
the contact sections

Let us now turn to the projection A'_H of this contact surface upon the plane HH , or, which is the same, the broken surface formed by the sections of the planes passing through

the pores (the dotted lines in Figure 32), the area of which is not taken into account, and the sections of the planes parallel to HH and passing athwart the contact sections, the total area being equal to A'_H . It is easily realized that surface A'_H is the minimum surface, and the corresponding stress σ_R is the maximum stress as compared to the stress at any other intersection. In the subsequent text, for brevity, the intersection by a broken surface (Figure 32) will sometimes be referred to as the contact section.

The pressure P from one solitary layer to the next is transmitted only through the surface of the contact sections of this layer. Hence, when considering the free-flowing body as a conglomeration of compact bodies (particles), it becomes possible, in accordance with formula (6/2), to write down:

$$A'_H = \frac{1}{\sigma_R} P \quad (16/1)$$

where σ_R is the critical stress, which is approximately constant within a certain pressure interval, A'_H is the projection of the contact surface of a horizontal solitary layer upon a horizontal plane. For further brevity, the magnitude of A'_H will be referred to as simply the contact surface of the solitary horizontal layer, or the contact section. The critical stress σ_R , as is the case in compact metals, coincides with the hardness of the powder metal under a corresponding degree of toughening, and is very close to its Brinell and Vickers hardness values.

Thus, we are justified in extending the principle of proportional limit to the contact surface of horizontal solitary layers, which are perpendicular to pressure.

It follows from formula (16/1) that the surface of any solitary horizontal layer is the same (if the losses of fracture to friction against the walls of the press mold are disregarded).

In the elastic deformation of cast metals, the cross section changes so insignificantly that it can be regarded practically as constant, while the stresses change in direct ratio to the external load. In the non-reversible deformation of powder briquettes, on the contrary, in conformance with formula (16/1), the stresses (if toughening is disregarded) are practically constant, and the area of the contact section A'_H varies in direct ratio to the load. This correlationship is only less usual but, by no means, more complex than the correlationship in the elastic deformation of compact metals. At any rate, it is simpler than the corresponding correlationship in the plastic deformation of compact metals, when both the stresses and the cross sections undergo changes.

17. Changes in the Structure and in the Physical State of

Powders Induced by Compression

Any (even the most insignificant) consolidation of powders promotes an increase in the contact surface of the particles and is accompanied by non-reversible deformation, which stipulates changes in the structure and properties of the powder

conglomerate.

The particles of certain powders, such as reduced copper, iron, nickel, cobalt, tungsten, are tied in by forces of cohesion into large agglomerates (paragraph 12, Figure 15). In pressing, such conglomerates are broken up into individual particles. If the bond between the particles of the agglomerate is weak, a mere pressure of several kilograms per square centimeter will be sufficient to break it. There occur, however, very tough agglomerates, which cannot be smashed even by pressures of several thousand kilograms per square centimeter.

In some cases, as a result of brittle deformation, not only the agglomerates of particles, but the particles themselves become disintegrated. This phenomenon occurs very frequently during the compression of non-metallic substances, while, in the case of metallic substances, its occurrence is less frequent, predominantly in powders with brittle and hard particles. Thin cast-iron chips are easily disintegrated by compression. Abrasive wear, manifested by the splitting-off of surface sections of the particles, is also linked to brittle deformation.

Plastic deformation of particles increases with the softness and plasticity of the metal and with the compression pressure. Maximum deformation is manifested by lead and tin, minimum deformation, by carbides of the refractory metals. Plastic deformation of the particles is localized in the sections of mutual contact which are subject to maximum stress equal to the σ_R -value. The deformed volume increases more

rapidly than the contact surface (see paragraph 8); hence, deformation and toughening during compression increase progressively, embracing ever larger areas and extending from the surface into the depth of the particles. Figure 33 shows the particles of granulated copper powder compressed under a pressure of 40 kilograms per square millimeter to a 25 percent porosity. At first, the particles were spherical in shape. The microphoto shows that deformation was localized in the places of contact, as a result of which the particles acquired the shape of polyhedrons. Figure 34, as per Goetzel, is a microphoto of a copper powder briquette with a twinning structure. The planes of twinning, which, prior to compression, were absolutely flat, were considerably curved out. This photograph shows clearly that plastic deformation extends from the contact surface into the depth of the particles.

Microphoto

Figure 33. Granulated copper powder briquette. Magnified x 500

Microphoto

Figure 34. Briquette made from electrolytic copper powder (as per Goetzel). Compression pressure was 63 kilograms per square millimeter. Magnified x 500

As a result of compression, the surface roughness of the particles also changes. The author's experiments with the adsorption of pigments on powder surfaces, prior to compression and after compression and pulverization, have revealed a dimin-

7

ution of the specific surface after deformation. The increase in the pouring weight of compressed powders (see Table 13) also indicates, in most cases, a diminution in roughness. However, if the initial powders had sufficiently smooth particles (as, for instance, of regular spherical shape), compression, on the contrary, may induce an increase in roughness and in the size of the specific purpose.

Compression induces a reduction in both interparticle as well as intraparticle porosity, it being the case that the largest pores, above the size of the particles are filled first.

Deformation is tied in with the toughening of powders. Trzebiatowski established the presence of all the indications of toughening by X-ray examinations and by hardness determinations of copper briquettes compressed under a pressure of 300 kilograms per square millimeter to a porosity of 3 percent. Debyeograms [Debye crystallograms] reveal all indications of cold-hardening, namely: the disappearance of the Van-Arkel splitting of the return lines, the expansion of the interference lines, the increase in diffused radiation. The indications of cold deformation disappear only with an increase in temperature. The hardness of the copper briquettes compressed under a pressure of 300 kilograms per square millimeter attained a value of 180 Brinell units, while the maximum hardness of deformed cast copper, as determined by Moore, was only 130 Brinell units.

In the deformation of compact metals, the change in the

overall shape. For example, when the overall cross section of a compact metal body is reduced by several times, the corresponding cross section of the crystals is reduced by the same number of times. Hence, the orientation of the crystals is clearly manifested in deformed metals.

A study of the structure of briquettes reveals that the compressing of free-flowing bodies basically is due not to the compressing of the particles themselves, but to their mutual displacement and sliding.

Footnote. The fact that compression in a number of cases causes the disruption and displacement of the previous contact between particles already follows from the breaking up of particle agglomerations. An analysis of the electrical conductivity of briquettes (see paragraph 39) confirms the same.

A metallographic study by the author of powders with equiaxial particles (non-compressed as well as powders compressed to various densities and to a porosity ranging from 10 to 15 percent inclusive) revealed the following:

(1). No extensive flattening of particles in the direction of compression and departure of particles from equiaxiality was noticed (Figure 35). The deformation of the particles was localized predominantly in the places of mutual contact.

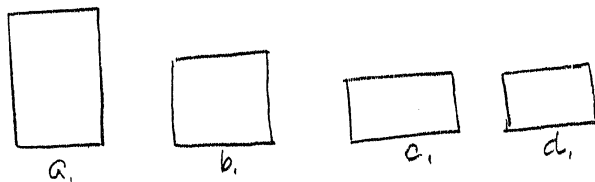


Figure 35. Consolidation diagram: a. initial porosity 50 percent; b. porosity 25 percent; c. porosity zero percent; d. consolidation due to the deformation of the particles themselves in the direction of compression.

(2). In compressing, the number of particles per unit of the micro-slide area (for both the transverse and longitudinal cross section) was increasing in direct ratio to the density of the briquette. The number of particles per unit of length was also varying in proportion to density. This experimental data coincides with the theoretical assumptions by the author relating to compressing by the filling of the pores, with the displacement of the particles. Diagram in Figure 35 a,b,c shows such a displacement of particles at the expense of filling up the pores, in the presence of which the number of particles per unit of volume, area, and length is increased in direct ratio to density. For purposes of comparison Figure 35,d shows the change in the number of particles due to the deformation of the particles themselves in the direction of compression. As can be seen, the number of particles in a longitudinal direction (the direction of compression) is in proportion to density (in an inverse ratio to height), and in a transverse direction -- in proportion to the square root of density. From diagram 35 (a,b, and c)

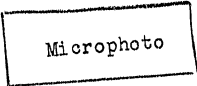
it follows that, in a briquette, the volumetric and surface porosity (the quota of pores for the cross section area) and the linear porosity (the quota of pores per unit of length) are mutually equal.

The absence of crystallographic orientation of the particles in compressed briquettes is linked to this nature of deformation of free-flowing bodies (regardless of the presence of structural orientation). X-ray examinations by Trzebiatowsky⁽¹⁵¹⁾ revealed the absence of texture in copper briquettes compressed under 300 kilograms per square millimeter to a practically compact state (porosity only 3 percent). Thus, the particles of the powder are subject to a sort of magnified pressure.

Already in the free pouring of the powder, the particles orientate themselves, i.e., they dispose themselves with their wider and flatter cross section normal to the force of gravity. Compression makes this orientation even more pronounced: with the narrow cross section in a longitudinal direction (the direction of pressure), and with the wide cross section in a transverse direction.

In compressed bodies, there is not only an orientation of particles in relation to direction, but also a surface orientation. In the surface layers of briquettes, the particles are disposed predominantly with their wider side parallel to the surface (at the sides as well as at the faces).

The orientation of particles with non-equiaxial cross sections can be observed in the microphotos of briquettes (Figure 36,b), as well as in some cases of fractures of already baked products.

(a)  Microphoto

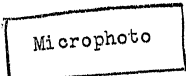
(b)  Microphoto

Figure 36. Briquette from electrolytic tin powder, relative density 80 percent, magnified x 500: a. transverse cross section; b. longitudinal cross section; shows the direction of compression.

Figure 37 shows fractures in baked copper moldings having flat particles (copper ore concentrate slimes on the left) and more equiaxial particles (electrolytic copper on the right). The copper concentrate slimes show a lamellate cleavage with an orientation of the lamina normal to compression.

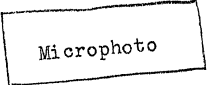
 Microphoto

Figure 37. On the left, a lamellate cleavage; on the right, a finely granular fracture.

Not only the particles, but also the pores in the briquettes, are orientated with their wider cross section normal to the direction of pressure. Figure 38 shows the orientation of the pores in a briquette made from copper powder with flat particles (copper concentrate slimes). In most cases, both the total

porosity and the cross section of individual pores (consequently, also their permeability) are lower in value in a longitudinal direction.

Microphoto

Figure 38. Briquette (longitudinal cross section) from copper concentrate slime; density 80 percent; magnified x 500; shows the direction of compression.

The size of the contact surface in a transverse (normal to compression) direction is greater than in a longitudinal direction.

As a result of compression, the volumetric characteristic of a powder changes. The pouring weight of a compressed and re-disintegrated powder, particularly in the case of soft powders, becomes increased (see Table 17). This increase in pouring weight is due to the diminution in the toughness of the surface oxidation layer, that was cracked during the first compression, and to the better packing of the particles (the breaking up of agglomerations, the formation of fragments, disposing themselves in the interspaces between large particles, the adaptation of the shape of the particles to mutual contact and the like). This increase in pouring weight grows with the degree of deformation, becoming higher with pressure. Sometimes, as in the case of tungsten (see Table 17), the pouring weight of the powder will be decreased, most probably at the expense of increased dispersion in com-

pression.

In the process of compression, the surface oxides and contaminations may be stripped off. The elimination of admixtures from the particle surface may result in frictional oxidation, which is promoted to a certain degree by the increase in temperature caused by friction.

TABLE 17

The Effect of Compression upon the Pouring Weight of a Powder

Kin Kind of Powder	Charac- teristic of Powder	Compression pressure (kg/sq cm)	Pouring weight in gr/cu cm	
			Prior to com- pression	After com- pression
Electrolytic copper	Soft	2000	1.50	2.07
Same as above	Soft	2500	1.50	2.17
Same as above	Soft	2500	2.47	3.28
Electrolytic iron	Soft	2500	2.11	2.65
Tungsten, reduced	Hard	2500	4.52	4.33

The particles, distributed in the charging mixture homogeneously, may be redistributed in the compressed semifinished product in a non-homogeneous manner, both by dispersion and by composition, due to the difference in deformability and "yield". This phenomenon, which is a sort of "liquation", is more strongly manifested at low rates of compression.

18. Compression Pressure

The expenditure of pressure for the compression of a powder is made up of three components (6).

(1). Pressure, p_1 , required for the consolidation of the powder, with the uniform distribution of pressure and density in all places of the briquette and the absence of losses to the external friction of the particles against the walls of the press mold; this component of pressure can be called net pressure.

(2). Loss of pressure, p_2 , to the external friction of the particles against the walls of the press mold.

(3). Excess pressure, p_3 , induced by the non-uniform distribution of pressure and density at the various places of compression.

The total pressure of compression $p = p_1 + p_2 + p_3$ may be designated the gross pressure or the full compression pressure.

It must be particularly emphasized that the loss of pressure to the internal friction of the powder particles against each other does not enter the pressure formula. For instance (see Figure 39), out of a full compression pressure of 10 tons, let 4 tons be lost to the external pressure against the walls of the press mold, leaving only 6 tons for the consolidation of the briquette. These 4 tons, lost by the briquette, are localized somewhere else, namely against the walls

of the press mold, and, onto the press table, is transmitted the full compression pressure of 10 tons as follows: 6 tons through the briquette, and 4 tons through the press mold matrix. However, if in some spots of the briquette four tons will be lost not to external, but to internal pressure, they will "be found" in other spots of the same briquette. One would not designate as a loss the shifting of money from one pocket into another. By the same token, there is no such thing as a loss of pressure to internal friction.

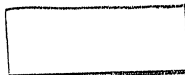


Figure 39. Diagram pertaining to the loss of pressure to friction

Further down in the text (paragraph 30), it will be shown that the reduction in pressure brought about by the addition of lubricants to the powder is due entirely to a reduction in external, but not internal friction. It is necessary, however, to remember that, although it is not expedient to discuss losses to internal friction, it nevertheless exists and even exerts some indirect effect upon the pressure increase. The non-uniform distribution of density along the cross section of the briquette, which induces an excess pressure, is linked to a considerable degree with internal friction in the powders. But this effect is relatively small. Although the internal friction surface of the briquettes is immeasurably greater than the external surface (sometimes, by millions or even billions of times), the excess pressure is usually very small as com-

pared with the pressure losses to external friction.

This chapter is devoted to the analysis of the net pressure. The other pressure components are discussed in Chapter V. In the consolidation of small briquettes (with a "reduced" height of 2 to 3 millimeters and a diameter of 10 to 15 millimeters), the full pressure practically coincides with the net pressure (it probably is only by 2 to 10 percent in excess of the net pressure).

19. The Ratio between Net Pressure and Deformation in the
Compressing of Powders

The ratio between elastic deformation and the tensile or compressive normal stresses in a compact metal is subject to the very simple Hooke's law. In this case, the infinitesimal increment in deformation is in direct ratio to the infinitesimal increment in stress:

$$d\sigma = \frac{dP}{A} = \pm k dh, \quad (19/1)$$

where P is the load,

A is the cross section area,

$\sigma = \frac{P}{A}$ is the stress,

h is the length (height) of the body

dh is the infinitesimal deformation increment,

k is a constant coefficient.

The formula for Hooke's law in the form of a differential equation (19/1) is the most convenient, since in this form, the above law is also effective for the case when A is not a constant. If the effect of cold-hardening is disregarded, formula

(19/1) is effective also in the case of plastic deformation of a compact metal.

The ratio between the pressure and non-reversible deformation is just as simple in the case of compressed metal powders. Let us analyze the consolidation of a briquette with a "reduced" height h_R in a cylindrical press form. Under load P , the briquette has a height h (Figure 40). When the pressure is increased by dP , the height of the briquette is reduced by dh . The stress in the powder briquette (see paragraph 16) is determined by dividing the load P by the area of the "contact" cross section A'_H . The direct ratio between the increment in stress and deformation will be expressed in this case by the formula

$$d\sigma = \frac{dP}{A'_H} = -\kappa dh \quad (19/2)$$

where κ , if the cold-hardening effect is disregarded, is a constant coefficient of proportion.

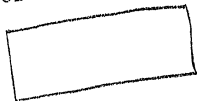


Figure 40. Diagrammatic representation of briquetting

The coefficient κ in formulas (19/1) and (19/2) depends on the initial length (height) h_0 . In order to render the coefficient of proportion, in the case of compact metals, independent of dimensions, the practice of relating deformation to the initial length (height) is accepted.

We then obtain:

$$\frac{dP}{A} = \pm E \frac{dh}{h_0}, \quad (19/1a)$$

where E is the constant coefficient, independent of the dimensions of the specimen, the so-called modulus of normal elasticity (Young's modulus).

The same independence of the coefficient from the dimensions of the briquette can be attained by dividing dh in the equation (19/2) by the initial height of the poured powder h_0 . Also, it is convenient, in place of the total pressure p per unit of the nominal transverse section of the briquette, We obtain:

$$\frac{dp}{A'_H} = -K' \frac{dh}{h_0} \quad (19/2a)$$

where K' , if the effect of toughening is disregarded, is a constant coefficient, similar, in a certain degree, to Young's modulus.

It is practically more convenient to adapt dh not to the initial height of the poured powder, but to the "reduced" height of the briquette h_k , i.e., to its height at 100 percent density (zero porosity), then:

$$\frac{dp}{A'_H} = -K'' \frac{dh}{h_k} = -K'' d\beta, \quad (19/3)$$

where β is the relative volume of the briquette ($\frac{dh}{h_k}$ can be substituted by $\frac{d\beta}{\beta}$, since, with the permanent cross section of the briquette, the volume changes with the height), and

$$K'' = \frac{h_k}{h_0} K' = \frac{K'}{\beta_0} = \mathcal{Q} K', \quad (19/4)$$

where β_0 is the relative volume
 ρ_0 is the relative density of the powder prior to compression.

In briquetting, it is not the entire volume that is subject to deformation, but only the volume that is occupied by the pores. Therefore, deformation may be related not to the initial or final ("reduced") volume (height), by the initial volume of the pores. In this case:

$$\frac{dp}{A'_H} = -K''(\beta_0 - 1) \frac{d\beta}{\beta - 1} = -K \frac{\beta}{\beta - 1}, \quad (19/5)$$

where

$$K = (\beta_0 - 1)K''$$

Formulas (19/2), (19/2a), and (19/3) are not convenient since they contain the magnitude of the "contact" cross section A'_H . Substituting into formula (19/3) in the place of A'_H its value $\frac{P}{\sigma_k}$ from formula (16/1), where σ_k is the critical stress, we derive:

$$\frac{dp}{P} = -\frac{K''}{\sigma_k} d\beta = -l d\beta = -l d\varepsilon, \quad (19/6)$$

$$\text{where } l = \frac{K''}{\sigma_k}$$

$\varepsilon = \beta - 1$ is the coefficient of porosity (see paragraph 14).

The magnitude l in the previous theses by the author^(2,10) was designated as the compression modulus. At this time, the author considers it preferable to designate as the compression

modulus the magnitude K from formula (19/5). Modulus K is linked to magnitude l by the following formula:

$$K = (\beta_0 - 1) l \sigma_R = \epsilon l \sigma_R \quad (19/7)$$

Magnitude l , as one of the cofactors of modulus K may be designated as the compression factor, and K'' as the "reduced" compression modulus. The magnitude of the compression factor l , if the cold-hardening value is disregarded, is constant (since, not even to mention β_0 , in this case K, K'' and σ_R are independent of the pressure). Under these conditions, pressure does not affect the value of l , and the properties of the powder metal σ_R affect it little, but it strongly depends on the volumetric characteristic of the powder (see paragraph 23), as per formula:

$$(\beta_0 - 1) l = \text{const.} \quad (19/8)$$

Actually, the phenomena of cold-hardening are very important, and, therefore, l, K'', K and σ_R are perceptibly dependent on pressure. Hence, even formula (19/8) lacks precision. According to an approximated evaluation in a number of cases $(\beta_0 - 1) l$ equals 4 -- 7, thus making the value of the compression modulus 4 -- 7 greater than the value of σ_R . If the cold-hardening effect is disregarded, the compression modulus will depend on the composition of the material only σ_R , but not on the physical characteristics of the powder and pressure. In this respect, there is a

certain analogy between Young's modulus and the compression modulus.

Substituting into formula (19/5), in the place of $\frac{dP}{P}$, the ratio $\frac{dA'_H}{A'_H}$, which is equal to the former, we obtain:

$$\frac{dA'_H}{A'_H} = -l d\beta \quad (19/9)$$

On the basis of formulas (19/5) and (19/9), the value of l as a factor indicating by how many times the relative increment of the contact cross section $\frac{dA'_H}{A'_H}$, or the relative increment of pressure $\frac{dP}{P}$, is greater than the reduction in relative volume $d\beta$.

By integrating the differential equation (19/5), we obtain:

$$\ln p_{\max} - \ln p = L(\beta - 1) \quad (19/10)$$

where $p_{\max}$ is the specific pressure corresponding to the maximum degree of consolidation, when $\beta = 1$.

Proceeding, for the sake of convenience, from natural to decimal logarithms and remembering that $\ln x = \frac{\log x}{\log e}$, where e is the natural logarithm base, we derive:

$$\log p_{\max} - \log p = L(\beta - 1) = L\varepsilon \quad (19/10a)$$

where

$$L = \log e \cdot l = 0.434 l \quad (19/11)$$

Equation (19/10a), represented graphically in coordinates of relative volume and the logarithm of specific pressure, is shown by a straight line in Figure 41 below. The straight line is characterized by two parameters. As the first parameter, it is best to take a point corresponding to $\lg p_{\max}$, as the second parameter, the tangent of the angle of inclination to the x-axis, which is equal to the compression factor L .

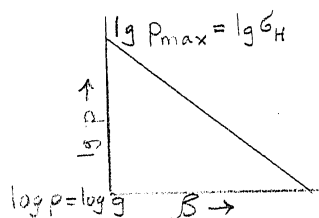


Figure 41. Ideal compression diagram

The value of $\lg p_{\max}$, in the case of net pressure, i.e., in the absence of pressure losses and excess pressure, can be determined with facility. With the maximum degree of consolidation, the area of the "contact" cross section equals the entire area of the transverse section, in this case, unity (since to a specific pressure $p_{\max}$ corresponds a cross section equal to unity). It being the case that the pressure $p_{\max}$, requisite to bringing the briquette to full compactness $\beta = 1$, obviously equals the critical stress σ_k (see paragraphs 6 and 16). If specific pressure (and σ_k) is measured in kilograms per square millimeter, then:

$$p_{\max} = \sigma_k = H_M \approx H_B \approx H_V. \quad (19/12)$$

where H_M is the Meyer hardness,
 H_B is the Brinell hardness,
 H_V is the Vickers hardness (σ_R -value is a little greater, by 5 to 20 percent, than H_B and H_V).

Hence, both the compression equation and the value of the constant σ_R essentially follow almost directly from the definitions of the terms "contact surface" (see paragraph 2) and "contact cross section" (see paragraphs 6 and 16).

By integrating the differential equation (19/8), we derive:

$$\log A - \log A'_H = \log \frac{A}{A'_H} = l(\beta - 1) = l\varepsilon \quad (19/13)$$

where A is the nominal area of the transverse section of the briquette (or, what is the same, the area of the "contact" cross section at 100 percent consolidation, when $\beta = 1$;
 A'_H is the area of the "contact" cross section.

Having familiarized himself recently with scientific data pertaining to the soil and to textiles, the author realized that, in the derivation of formula (19/9), insofar as it relates to soil compression, he was preceded by Tertsagi⁽⁶²⁾. Sommer⁽¹⁴⁴⁾ established a similar ratio in the consolidation of textile materials about the same time the author arrived at his formula with relation to metal powders. These men derived the analogous formulas empirically (and not on the basis of theoretical premises, and they did not clarify the nature of the constant σ_R of the law of compression.

20. Tangible Compression Diagrams: Relative Volume -- the
Logarithm of Specific Pressure

Figure 42 below shows a rather typical tangible compression diagram obtained in a Gagarin press, in the case of an electrolytic copper powder with a pouring weight of 1.42 grams per cubic centimeter. The diameter of the briquette was 9.25 millimeters, its reduced height h_A was 2 millimeters. Due to the small dimensions of the briquette, the pressure losses to external friction and to excess pressure can be disregarded. The final porosity, at a specific pressure of 69 kilograms per square millimeter is 8 percent.

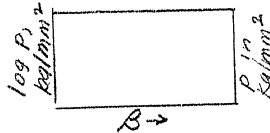


Figure 42. Typical tangible compression diagram

As can be seen in Figure 42, the tangible compression diagram is curvilinear, and the compression factor $L \neq$ constant. The non-constancy of the value of the compression factor L is due to the change in the properties of the powder during the process of compression. The value of factor at any point of the tangible diagram in Figure 42 is determined by the tangent of the angle formed by a line tangent to the curve at this point with the x-axis. In this case, the curve is facing with its convexity downward, and the factor is all the time increasing.

Let us draw a line tangent to the curve in Figure 42,

at a point corresponding to a specific pressure $p = 3.4$ kilograms per square millimeter, and a relative volume $\beta = 2.5$. The tangent of the angle formed by this line with the x-axis (0.68) equals the compression factor L at the given degree of compressing reduction. If, with the increase in the degree of pressure, the properties and the critical stress σ_k of the powder would remain constant, the value of L would at all times be equal to 0.68. Therefore, the point of intersection of this tangent line with the ordinate $\beta = 1$, may be accepted as the logarithm of the critical stress corresponding to the point of tangency.

In table 18, the graphically plotted value of σ_k and L for the points in the curve in Figure 42, at low, medium, and final pressure, are cited.

TABLE 18

Ratio between the Value of Critical Stress σ_k and the Degree of Compressing Reduction (Diagram in Figure 42)

No. in sequence	Characteristic of the degree of compressing reduction			Compression factor	σ_k in kg/sq mm
	Specific compression pressure in kg/sq mm	Relative volume of briquette	Porosity in percent		
1	3.4	2.5	60	0.68	36
2	10.7	1.82	45	0.88	56
3	69	1.089	8	1.39	88

As indicated above, the value of the critical stress σ_R of the material coincides with its Meyer hardness, the latter being somewhat greater (by 5 to 20 percent) than the Brinell hardness of the material.

Hence, the σ_R -value, for example, at a specific pressure of 10.7 kilograms per square millimeter corresponds to the hardness the material would possess under conditions of a compressive reduction from a porosity of 45 percent to a completely compact state without any further change in properties. This macro-hardness approximately corresponds to the microhardness of the powder particles in their places of mutual contact at a given degree of compressive reduction. In the first stages of compressive reduction σ_R equals 36 kilograms per square millimeter, which corresponds to the conventional hardness of non-toughened copper. At the stage of compressive reduction when the porosity of the briquette is 45 percent, the σ_R -value equals the hardness of the metal in its medium degree of toughening (56 kilograms per square millimeter). Finally, the critical stress under the high stages of compressive reduction is close to the hardness of copper in its maximum degree of toughening.

Thus, the variations in the values of the compression factor and of the critical stress in the diagram, presented in Figure 42, can be understood, if the cold-hardening effect of the metal, with the increase in compressive reduction, is taken into account.

Let us now compute the errors that occurred in the

determination of the σ_R -value as 88 kilograms per square millimeter for a porosity of 8 percent. Basically, these errors are reduced to the following.

(1). The value 88 kilograms per square millimeter is somewhat greater than the real σ_R -value on account of losses to external friction. Also, the σ_R -value is somewhat increased due to the imperfect uniformity of density distribution along the cross section and height. It may be assumed that these factors induce an increase in the σ_R -value, as against the real, by approximately 5 percent.

(2). In the computation, the specific gravity of copper was taken as 8.93. According to Hanson, Mariat, and Ford, the density of rolled copper, containing 36 percent oxygen, is 8.75 grams per cubic centimeter, i.e., by 2 percent lower than the computation value. The powders involved had a content of 0.5 percent oxygen, as a result of which the departure of the actual specific gravity from the 8.93 value amounted to about 2 or 3 percent. The error caused by it results in an increase of the σ_R -value by approximately 10 percent.

(3). The elastic expansion of the briquette after the pressure was removed resulted in an increase in volume by about 1 percent. The σ_R -value computed by the volume, "reduced" as a result of the elastic aftereffect, is in this case by approximately 4 percent greater than the σ_R -value determined by the "non-reduced" volume. However, this difference may be dis-

regarded, inasmuch as the conventional determinations of hardness are also conducted with "reduced" impressions.

Thus, the σ_R -value as equal to 88 kilograms per square millimeter, under a compressive reduction of 92 percent, is determined with an excess error of about 10 to 15 percent. Hence, it can be considered as approximating the σ_R -value under maximum compressive reduction to a relative density of 100 percent.

21. The Further Study of the Semilogarithmic Compression Diagrams

The semilogarithmic compression diagrams for several metal powders are shown in Figure 43. The values for the critical stress σ_R and the compression factor L in the case of various metal powders are compiled in Table 19.

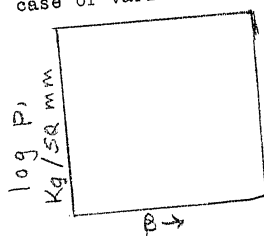


Figure 43a. Semilogarithmic compression diagrams for powders: 1. electrolytic tin, pouring weight 1.02; 2. electrolytic iron, pouring weight 2.70; 3. tungsten, reduced, pouring weight 4.18

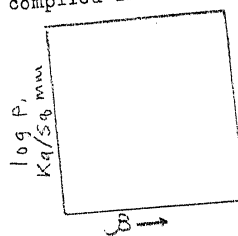


Figure 43b. Semilogarithmic compression diagram for a baked copper product with an initial porosity of 43 percent

TABLE 19

 σ_R and L Values for Some Powders

No. in sequence	Type of powder	Powder characteristics			σ_R in kg/mm ²				Initial		Final	
		Pouring weight in grams/cm ³	Relative density of powder charge in %	Size of particles in microns	initial	final	initial	final	P, in kg/mm ²	σ	P, in kg/mm ²	σ
[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]
1	Tin, electrolytic	1.10	15.1	10-60	4.8	46	0.19	2.46	2.6	3.0	25	1.14
2	Tin, pulverized	3.50	48	60	3.2	40	0.45	13.3	1.4	1.8	40	1.00
3	Lead, pulverized	3.98	35.3	60	4.2	38	1.04	10.0	1	1.6	23	1.03
4	Copper, electrolytic, fine	0.97	10.8	10	48	100	0.65	1.05	2.4	2.6	75	1.08
5	Copper, electrolytic, medium	1.42	15.9	10-30	36	88	0.68	1.39	3.4	2.5	69	1.08
6	Copper, electrolytic, coarse	2.47	25.4	20-60	48	100	1.10	1.50	2.5	2.18	89	1.07
7	Copper, MOZ, obtained by the											

[continued on next page]

	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]
reaction of wood shavings with copper sulphate	3.51	39.3	10-30-	630	63	2.42	1.80	1	1.95	50	1.06		
8 Copper, spherical granulated, non-annealed	4.50	50.4	30-60	500	85	3.27	1.28	1.6	1.72	63	1.08		
9 Copper, spherical granulated, annealed in hydrogen at 600°C	3.92	43.9	30-60	70	70	1.40	1.40	1.6	2.13	63	1.04		
10 Iron, fully reduced at 700°C, 60 minutes	0.18	2.3	1-5	5	105	0.20	0.93	1.8	4.10	63	1.23		
11 Iron, partly reduced at 700°C, 10 minutes	0.24	3.5	1-5	700	330	1.74	1.61	2.0	2.90	63	1.48		
12 Iron, reduced at 700°C, 30 minutes	0.21	3.3	1-5	442	440	1.03	1.46	2.0	3.26	63	1.59		

[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]
13 Iron, fully reduced		0.67	8.5	5-10	19	98	0.32	0.9	2.7	3.81	69	1.18
14 Iron, electrolytic, annealed	2.70		34.2	60	65	78	1.60	1.96	1.0	2.15	50	1.10
15 Iron reduced from the ore, at 850°C	1.65		20.9	10	140	140	1.06	1.06	3.2	2.56	63	1.33
16 Iron, white	--	--		60	--	580	--	1.78	--	--	63	1.54
17 Iron, white, annealed at 800°C	--	--		60	--	285	--	1.56	--	--	63	1.39
18 Iron, white, annealed at 1000°C	--	--		60	--	150	--	1.40	--	--	63	1.27
19 Semi-steel, thin brittle chip, acicular	1.10		15.1	3000	55	130	1.00	1.52	1	2.85	63	1.20
20 Semi-steel, fine non-brittle chip	1.98		27.1	500 - 1000	200	200	1.66	1.66	1	2.41	63	1.30
21 Tungsten, reduced	4.18		22	1-5	1000	235	1.80	1.10	3.17	2.38	63	1.52
22 Tungsten carbide	--	--		1-5	1150	1580	2.92	3.10	1	2.06	63	1.45

Note. Most of the powders contained up to 0.5 percent of oxygen. No corresponding corrections to the specific gravities of the pure metals were introduced into the computation of the relative volumes of the briquettes. Hence, the values of the relative volumes σ_R and L are somewhat in excess of the actual values. The σ_R and β values are taken by the aftereffect -- "reduced" volumes (the difference between the σ_R values, by "reduced" and "non-reduced" volumes, are in most cases less than 2 -- 4 percent). Corrections for the change in specific gravity as a result of oxidation were introduced only for the partly-reduced iron No. 11 (the degree of reduction 51.7 percent), and for No. 12 iron (degree of reduction 53.9 percent.)

For a number of powders, the σ_R -values in the first stages of compressing reduction are close to the hardness of non-toughened metal. For instance, in electrolytic tin, $\sigma_R = 4.8$ kilograms per square millimeter; in pulverized tin, 3.2 kilograms per square millimeter; in pulverized lead, 4.2 kilograms per square millimeter; in electrolytic copper, from 36 to 48 kilograms per square millimeter; in electrolytic iron, 65 kilograms per square millimeter.

In some light-weight and fine powders, the σ_R -value is many times below the hardness of the non-toughened metal. For instance, in reduced iron powder with a pouring weight of 0.67 grams per cubic centimeter (the relative density of the poured charge is 8.5 percent), under a specific pressure of $\rho = 2.7$ kilograms per square millimeter and a relative

volume $B = 3.81$ (the porosity of the briquette is 74 percent), $\sigma_k = 19$ kilograms per square millimeter. The initial value of σ_k is still lower in the case of a fine light-weight reduced iron powder with a pouring weight of 0.18 grams per cubic centimeter (the relative density of the poured charge $\rho = 2.3$ percent). This powder, under a specific pressure of 1.8 kilograms per square millimeter and a briquette porosity of 76 percent, has a compression factor of 0.20 and a critical stress of 5 kilograms per square millimeter, which is rather close to the hardness-value of non-cold-hardened tin.

Such low initial values of the critical stress σ_k for metal powders with a low pouring weight are due to the following.

(1). The particles of such loose powders undoubtedly have considerable internal and "surface" porosity (see paragraph 13). The critical stress is determined by the hardness of the contact sections of the particles, the value of which is lowered considerably by such porosity. For instance, the baked iron filling compounds with a 60 percent porosity, prepared by the author, had a Brinell hardness, prior to the compressing reduction, of 3.5 to 4 kilograms per square millimeter, the same as lead. However, after the compressing reduction in the press, they had the hardness of pure cold-hardened iron, which is 70 to 90 kilograms per square millimeter.

(2). In the case of powders with a high degree of dispersion (see Figure 24), the exceptionally low hardness of the very external moisture-containing "argyllaceous" layer of oxides on the surface of the particles may be of some importance

(the deeper layers of the "dry" oxides, on the contrary, are harder than the basic metal). In addition, the contact sections of the small particles should be less toughened and less hard than in the case of large compact bodies. Let us point out that as per experiments by O'Neil⁽⁴⁷⁾ Henriot⁽⁹⁶⁾, Harris⁽⁴⁷⁾, Krupkovskiy⁽¹¹⁸⁾, and others, in the complete absence of cold-hardening on the impressions, hardness is approximately three times below the conventional values for the non-toughened metal, and is rather close to the value of the yield point.

Heavy powders have a higher initial σ_R -value. Electrolytic iron with a pouring weight of 2.70 grams per cubic centimeter, under a specific pressure $p = 1$ kilogram per square millimeter, has a value of $\sigma_R = 65$ kilograms per square millimeter. In granulated annealed copper the initial value $\sigma_R = 68$ kilograms per square millimeter. Seemingly, the heavy particles, even prior to compression, sustain a greater cold-hardening effect at the contacts than the lighter particles. In paragraph 13 (Figure 28), it was pointed out that the consolidating moment, stipulated by the very weight of the particles, grows in a direct ratio to the diameter of the particles raised to the fourth power, and to their weight raised to the power $4/3$.

Some powders manifest very high initial σ_R -values, that are considerably in excess of the hardness of the metal under a maximum degree of toughening. The initial critical stress of granulated non-annealed copper is 500 kilograms per square millimeter, same for tungsten is 1000 kilograms per square millimeter, for only partly reduced iron with a

pouring weight of 0.24 grams per cubic centimeter is 700 kilograms per square millimeter.

Such high initial values of σ_R are due principally to the presence of hard surface admixtures or to the greater hardness of the surface layer of the particles resulting from treatment. During the first stages of compression, it is usually the harder surface layer of the particles that sustains deformation. According to Holm⁽¹⁰²⁾, Khrushchev⁽⁶⁸⁾, and others, increased hardness values are observed under a very small load. To some extent, the high initial values of L and σ_R may be explained by the considerable role of elastic deformations at low pressures. This, specifically, is the circumstance, to which the high initial values of L under compressing reduction of already baked articles are attributable (see Figure 43,b).

The final σ_R -values approximate the hardness of the compact metals under a maximum degree of toughening.

Ackermann⁽⁷⁵⁾ introduced the term "pressure of outflow" to designate a stress, under which a cylindrical punch rapidly submerges into the metallic specimen being tested. O'Neil and Greenwood⁽¹²⁷⁾ offered the assumption that the stress of the extrusion of metal through an opening equals the pressure of outflow. According to O'Neil, the pressure of extrusion corresponds to the hardness of the metal at the maximum degree of toughening.

The values for the pressure of extrusion of various metals are cited in Table 20, in accordance with O'Neil.

These pressures are 1.5 to 3 times in excess of the Brinell hardness of non-toughened metals.

TABLE 20

Pressure of Emanation as per O'Neill

Metal	Pressure of	Brinell	Ratio between
	extrusion in kg/sq mm	hardness in kg/sq mm	pressure of ex- trusion and Brinell hardness
Lead	10	3.5	2.9
Tin	14	5	2.8
Aluminum	42	20	2.1
Silver	76	35	2.2
Gold	80	25	3.2
Copper	92 - 109	49	1.9 - 2.2
Soft iron	126 - 133	70	1.8 - 1.9
Steel (0.28% C)	180 - 195	--	--
Tungsten	400	240	1.7

In the case of the soft metal powders, the ultimate σ_R -values are higher, and in the case of the hard metal powders, they are lower than the pressures of extrusion. The causes of this phenomenon will be analyzed in paragraph 22.

Bridgeman⁽⁸⁴⁾ followed up with the illustration of compressing the metal to full compactness under the pressure of extrusion. Hollow copper pipes, sealed at both ends, were subjected to manifold hydraulic pressure. When the pressure

of extrusion (100 kilograms per square millimeter) was attained, the internal diameter of the pipes was reduced to zero.

In the case of very light powders, the values of the critical pressure σ_k and the factor L are increased greatly with the compression pressure. For instance, in an iron powder with a pouring weight of 0.18 grams per cubic centimeter, the σ_k -value rose from 5 kilograms per square millimeter to 105 kilograms per square millimeter and the value of the compression factor L rose from 0.20 to 0.93. This is basically due to three causes:

(1). The increase in the cold-hardening effect with compressing reduction.

(2). The increase in the hardness of the particles at the expense of the reduction in the intraparticle and "surface" porosity with compressing reduction.

(3). The increase in the coefficient of the lateral transmission of pressure E . Coefficient E increases in direct ratio to the relative density of the briquette (see Chapter V). With the increase in lateral pressure, the "wedging" between the particles becomes greater, resulting in a greater resistance of the briquette to compressing reduction.

The effect of these three causes is considerably attenuated in the case of the heavier powders, as follows:

The initial cold-hardening effect at the contacts, as

was already indicated, is considerably more pronounced in the case of the heavy powders. Hence, this effect, spread over the entire process, is less pronounced.

(2). The intraparticle and "surface" porosity of the particles is insignificant, and a perceptible increase in hardness due to the diminution in this porosity is not very likely to occur.

(3). The initial density of the briquette is considerably greater, as a result of which the increase in the coefficient of lateral pressure is less pronounced.

Hence, in the case of heavy powders, the values of σ_R and L increase with pressure less rapidly. The above noted decrease in the compression factor L with pressure in the very first stages of compression is, on the contrary, more pronounced in the case of the heavy powders.

The initial pressures for the attainment of the same briquette densities are always greater in the case of light powders than they are in the case of heavy ones. This is due to the higher "structural" toughness of powders with low pouring weight and their low density prior to compression. However, the ultimate pressures requisite for the attainment of 100 percent density for the various powders of the same metal are almost the same and approximately equal to the pressure of extrusion (see Figure 44). For this reason, the compression factor L in light powders of the same metal is greater than in heavy powders.

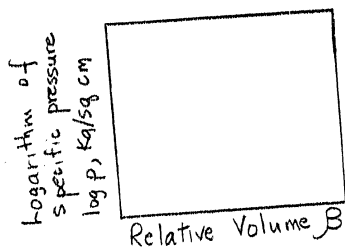


Figure 44. Semilogarithmic compression diagrams in relation to the pouring weight of copper powders: 1. electrolytic copper, pouring weight 0.97 grams per cubic centimeter; 2. same, with pouring weight 1.50 grams per cubic centimeter; 3. granulated copper, with pouring weight 4.50 grams per cubic centimeter.

It is also comprehensible that, with the same packing density, hard metal powders will have a higher compression factor than soft metal powders.

The recently published data by Steinitz relating to the determination of the microhardness of powder particles revealed that the hardness of the particles is rather close to the hardness values of the non-toughened compact metals and to the σ_R -values arrived at by the author. Thus, according to Steinitz, the hardness of the annealed electrolytic iron powders was 52 to 59 kilograms per square millimeter (as compared to the author's σ_R -value for electrolytic iron of 65 kilograms per square millimeter). The hardness of reduced iron powders, according to Steinitz, is 47 to 60 kilograms per square millimeter, of the incompletely reduced inclusions in the iron powder, 350 kilograms per square millimeter, as compared to the author's σ_R -value for the incompletely reduced iron powder of 330 kilograms per square millimeter. The hardness of powder steel, according to Steinitz,

is 750 kilograms per square millimeter, and after decarbonization annealing it is 260 and 168 kilograms per square millimeter (as compared to the author's σ_R -values for non-annealed white iron of 580 kilograms per square millimeter, and, after graphitization annealing, of 235 and 150 kilograms per square millimeter).

By the same token, the values for the critical stress σ_R and the compression factor, computed by the author from the data of Kieffer and Hotop⁽¹¹⁵⁾ for the compression of various powders under the specific pressures of 20, 40, and 60 kilograms per square millimeter, are also close to the results obtained empirically by the author. The results of the author's computations are cited in Table 21. On the whole, the ultimate σ_R -values, computed by the author on the basis of the data of Kieffer and Hotop, are somewhat higher than the ones obtained by the author independently. It is probably due to the fact that the experimental powder batches used by Kieffer and Hotop were somewhat larger than the batches used by the author, causing greater losses of pressure to external friction and excess pressure.

See next page for Table 21

TABLE 21

Critical Stress σ_R and Compression Factor L Computed by the Author from the Data by Kieffer and Hotop

Characteristic of powder, kg/sq mm								
No. in sequence	Type of Powder	Pouring	Particle size	σ_R		L		Ultimate rela-
		weight in gr/cu cm		initial	ultimate	initial	ultimate	tive density ρ in %
1	Silver, granulated	3.84	up to .3 mm	75	75	1.96	1.96	95
2	Silver, from AgCl	1.82	up to 30 μ	59	100	1.03	1.55	86.7
3.	Copper, electrolytic	1.25	up to 30 μ	98	98	1.23	1.23	84.5
4	Iron, vorticity mill	2.42	up to 0.4mm	104	152	1.44	1.87	83.0
5	Iron, carbonyl annealed	--	up to 5 μ	--	118	--	1.45	81.6
6	Same, but non-annealed	3.45	up to 5 μ	93	204	1.06	1.97	78.7
7	Tungsten, reduced	4.65	up to 5 μ	317	317	1.88	1.88	71.9
8	Tungsten, mechanically pulverized from baked molding	6.80	up to 50 μ	832	490	3.52	2.22	70.4
9	Same as above	--	up to .3mm	--	317	--	1.56	68.1

22. Compression Diagrams in Relation to the Type of Metal and Compression Temperatures

It was brought out in Chapters 20 and 21 that, in the absence of losses to friction against the walls of the press mold and with a uniform density of the briquette, the line tangent to the curve $\log p - \beta$ intersects the ordinate for $\beta = 1$ at a point corresponding to the critical stress σ_R of the material for the given density. This value of σ_R is approximately equal to the Meyer hardness of the particle contact sections at the given degree of compressing reduction. More specifically, the σ_R -value computed in this manner equals the Meyer hardness -- the material would have, if it were compressed from this degree of consolidation to a fully compact state without any further change in the hardness of the contact areas.

It may be assumed that the σ_R -values, as above determined, will, with briquette densities of 90 to 99 percent, almost equal the $\sigma_{R\max}$ value, i.e., the critical stress at the maximum degree of toughening, or practically equal the pressure of extrusion (see Table 20).

It follows from Table 19 that, in the case of soft metals, the maximum critical stress is considerably higher than the pressure of extrusion. The ultimate σ_R -values for tin are 46 and 40 kilograms per square millimeter, while the extrusion pressure is 14 kilograms per square millimeter; for lead, the ultimate σ_R -value is 38 kilograms per square millimeter, while the pressure of extrusion is 10 kilograms per square milli-

meter. For metals of medium hardness, such as copper and iron, the ultimate critical stresses σ_R , determined at briquette densities of 90 to 95 percent, almost equal the pressure of extrusion. The ultimate σ_R -values for copper oscillated within the range from 63 to 100 kilograms per square millimeter, with the extrusion pressure being 126-133 kilograms per square millimeter. For extremely hard materials, the maximum specific compression pressures were only a small part of its hardness value (25 percent of it in the case of tungsten and 5 percent in the case of tungsten carbide). Hence, it is difficult to make any assumptions relating to the value of the maximum critical stress characteristic of these materials.

It also follows from Table 19 that the values of the compression factor increase with consolidation more rapidly in the case of the soft metal powders (tin and lead) than in the case of the hard metal powders.

Some data compiled by the author on the change in the values of the specific compression pressure p , of the critical stress σ_R , and of the compression factor L with the increase in the degree of consolidation from 80 percent to 90 percent, for tin, lead, copper, and iron. All these values increase more rapidly in the case of soft metals.

TABLE 22

Ratios between the P , σ_R and L Values and the Relative Briquette Densities

Type of powder	Pouring weight in gr/cu cm	Relative density of briquettes in %	Specific pressure p		Critical stress σ_R		Compression factor L	
			condition-	al units	condition-	al units	condition-	al units
			$k_F/sq\ mm$		$k_F/sq\ mm$		$\frac{d\ \epsilon_{qp}}{d\ \beta}$	
Tin, electro-lytic	1.10	80	13	100	24	100	1.08	100
		90	25	192	46	192	2.46	228
Tin, pulverized	3.50	80	5.25	100	12.5	100	1.51	100
		90	10.5	200	18.7	150	2.30	153
Lead, pulverized	3.98	80	2.52	100	6.7	100	1.70	100
		90	6.31	250	11.3	169	2.30	135
Copper MOZ	3.51	80	22.5	100	62	100	1.80	100
		90	38	169	63	101	1.80	100
Copper, electro-lytic	1.42	80	41	100	81	100	1.20	100
		90	63	154	88	109	1.39	115
Iron, electro-lytic	2.70	80	28.2	100	78	100	1.96	100
		90	50	177	78	100	1.96	100

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At the first glance, these results may seem somewhat paradoxical. The temperature of compression (room temperature) for tin and lead is higher than the temperature of recrystallization, and therefore, it would seem, no perceptible toughening should occur. It can be seen, however, from Table 20 that the pressure of extrusion (i.e., hardness at maximum toughening) is 2.9 times greater than the hardness of non-toughened material, in the case of soft metals (lead and tin), 1.8 to 2.2 times greater in the case of metals of medium hardness (copper, iron), and 1.7 times greater in the case of metals of great hardness, such as tungsten. Hence, the compact soft and plastic lead and tin become toughened at room temperature to a greater degree than the hard and brittle metals. Numerous scientific writers, in their investigations of the hardness of compact metals, have shown that the maximum toughening of a metal occurs not at the lowest, but at comparatively high temperatures. According to Sauveur and Lee⁽¹³²⁾, iron and steel are at their maximum hardness when deformed in the temperature interval 200 to 400° Centigrade. Shwarz⁽¹³⁵⁾ revealed that the capacity to cold-hardening in soft steel is greater at the temperature of 300° Centigrade than at room temperature, and the hardness and capacity for cold-hardening in copper is greater at room temperature than it is at lower temperatures. Even before that Robin⁽¹²³⁾ established the fact that the capacity of metals for toughening is reduced when the temperature drops below room temperature. According to Robin, metals at absolute zero are not capable of perceptible toughening. Research conducted by O'Neil confirmed the deductions

arrived at by Robin.

Thus, it is altogether possible that the considerable increase in the resistance to deformation with the compressing reduction of soft metal powders is to a certain extent stipulated by cold-hardening. It must be remembered that the relatively high rate of compression and the high content of admixtures (specifically, in the contact sections) must substantially inhibit the detoughening of the powdered metal.

However, the increased resistance to deformation on the part of soft metal powders is not exclusively due to cold-hardening. It may be to no lesser, and perhaps even to a greater extent, induced by other factors. In Chapter VII we shall see that, under the same degree of compressing reduction, the toughness of soft and plastic metal powder briquettes is many times greater than that of hard and brittle metal powder briquettes. And the pressure requisite for a given degree of compressing reduction is specifically determined by the toughness of the briquette at this density.

Under a relative density of 80 percent, the bond between tin particles is much tougher than between copper or iron particles. Hence, the force required for the shearing action of the particles as per the diagram in Figure 29c (in the preceding text), must be greater in the case of tin and lead than in the case of copper and iron.

Footnote. It shall be shown in Chapter V and VII that the greater toughness of soft metals is stipulated to a considerable extent by a high Poisson's ratio value.

Jones (107) investigated the pressibility of iron, aluminum, and copper at room temperature and at low temperatures (-20 , -80 , -193° Centigrade). Regrettably, he does not furnish any data on the density of briquettes at low pressures, and his figures, in general, are not very specific. Semilogarithmic compression curves plotted by the author by the Jones data are shown in Figure 45. The assumed paths of the curves at low pressures is shown by dotted lines. The values for σ_R , P and h in the case of iron at various compression temperatures are given in Table 23.

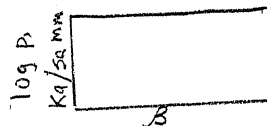


Figure 45. Semilogarithmic compression curves for iron at various temperatures (plotted by the author on the basis of Jones data)

[See next page for Table 23]

It follows from the Jones research that pressures required for high degrees of consolidation at various compression temperatures were not very much apart. The specific pressure for the compressing reduction of iron to a relative density of 90 percent at room temperature is 61.7 kilograms per square millimeter, and at minus 193° Centigrade it is 70.8 kilograms per square millimeter. The corresponding σ_R -values are 105 and 107 kilograms per square millimeter, respectively. During the first stages of compressing reduction, it takes several

TABLE 23

Values for σ_R , p, and L, at Various Compression Temperatures for Iron Powder (Based on the Jones Data)

Compres- sion tem- perature in °C	Specific pres- sure p, in kg/sq mm	Relative density ρ in %	Critical stress σ_R				Relative density, in %	Specific pressure, p		Critical stress		
			kg/sq mm	condi- tional		L		kg/sq mm	units	kg/sq mm	condi- tional	
				tional	tional						tional	units
+23°	8	62.5	42.7	100	1.22	62.5	8	100	42.7	100	1.22	
	24	78.7	66.8	156	1.65	80	27.5	344	77.7	159	1.80	
	48	87.0	100	285	2.13	90	61.7	771	107	256	2.30	
	64	90.9	107	286	2.30	--	--	-	--	-	--	
-192°	8	41.7	42.7	100	0.59	62.5	20.4	100	63	100	0.82	
	24	65.8	66.8	156	0.86	80	44.7	219	91.3	145	1.25	
	48	81.3	105	246	1.48	90	70.8	347	105	167	1.48	
	64	87.8	105	246	1.48	--	--	-	--	-	--	

times the above specific pressure to attain a relative density of 62.5 percent at minus 193° Centigrade, and the $\mathcal{R}$ -value, too, is considerably higher. The values of the compression factor L, under a higher degree of compressing reduction, also increase more rapidly at high temperatures. Hence, the conclusion that, with an increase in temperature, the resistance to deformation in compressing reduction grows more rapidly.

The phenomena observed with the increase in compression temperature are analagous to the changes in the capacity for deformation with reduced hardness in powders, and they can be explained in the same manner, i.e., by the increased toughness of briquettes with compression temperature.

The softer pure metals are the more easily fusible ones, hence, in their case, room temperature is closer to the temperature of recrystallization. Alloys may have a lower melting point at greater hardness than pure metals, however, their temperature of recrystallization is usually higher. Thus, room temperature, in most cases pertaining to softer metals, is closer to the temperature of recrystallization

Data by Schwarzkopf and Goetzel⁽¹³⁶⁾ pertaining to the value of specific pressure in the hot-pressing of iron powder (at 20, 600, and 1100° Centigrade) is presented in Table 24. It shows that the resistance to deformation, with the degree of compressing reduction increases more rapidly at higher compression temperatures.

TABLE 24

Values of Specific Pressure p in Relation to Relative Density
and Compression Temperature of Sponge Iron as per Schwarz-
kopf and Goetzel (the High Values Are Probably Due to
the Relatively Large Size of the Briquettes)

Relative density in %	20°C		600°C		1100°C	
	P		P		P	
	cond'l		cond'l		cond'l	
	kg/sq mm	units	kg/sq mm	units	kg/sq mm	units
90	160	100	16	100	3	100
95	240	150	30	188	6	200
100	350	212	47	294	11	366

23. Semilogarithmic Compression Diagrams in Relation to the
Volumetric Characteristic and Structural Factors

It was pointed out in paragraph 13 that the volumetric characteristic directly reflects the toughness of the powder -- its resistance to compressing reduction under the effect of its own weight. The lighter and the looser the powders, the greater their toughness.

In the first stages of compression, under insignificant pressures, the contact sections of the particles, assuming the entire load, are small in size. Hence, at the beginning of compression, the toughness of a powder at a given density, as determined by a pressure requisite for the attainment of such density, is a "structural" toughness, stipulated by the size, structure, surface relief, and the properties of the thin sur-

face layer of the particles.

In conformity with the above, the diagrams in Figure 44 and the data from Table 19 (see Paragraph 21) show that, in the first stages of compression, the pressures requisite for the compressing reduction of powders of the same metal to the same density, are different for powders with different pouring weights. For powders of low pouring weight, these pressures, equal to the toughness of the powder at the given density, are considerably greater than for heavy powders with higher pouring weights.

With increased pressure the deformed volume of the particles extends in width and in depth embracing ever greater areas. At a 100 percent-density of the briquette, the area of deformation may extend to the entire volume of the material. Therefore, with the increase in compressing reduction, the "structural" toughness becomes less and less important, and the toughness of the metal itself, more and more important. The compression diagrams of powders of the same metal, but with different volumetric characteristics (see Figure 44) show that, with the higher densities of briquettes, pressures requisite for the same degree of compressing reduction approximate, progressively, each other. At a 100 percent-density $\beta = 1$, the extensions of all the curves are intersected approximately at the same point on the ordinate axis (which, in this case, is the line drawn through the points, for which $\beta = 1$), the point corresponding to the maximum critical stress σ_k of the given metal, i.e., approximately to the pressure of extrusion. However, some differences in

the pressure value may remain even under very high degrees of compression reduction. It is possible that the volumetric characteristic of the powder has an effect upon certain maximum critical stress σ_R -value oscillations for the given metal. For example, in the case of copper MOZ with a pouring weight of 3.51 grams per cubic centimeter (see table 19), $\sigma_R = 63$ kilograms per square millimeter (below the pressure of extrusion); in the case of fine electrolytic copper with a pouring weight of 0.97 grams per cubic centimeter, $\sigma_R = 100$ kilograms per square millimeter (equal to the pressure of extrusion). It may be that the differences in the value of the maximum critical stress in these powders are caused by the volumetric factors, and that, in the case of the heavy MOZ copper powder, the toughening, when $\psi = 100$ percent, does not extend to the entire volume, while in the lighter electrolytic copper, it does involve the entire volume. It is, nevertheless, possible that a certain effect is exerted by the surface admixtures, of which there is more in the light high-dispersion powders of electrolytic copper.

In the absence of a cold-hardening effect (see Figure 41), it would be simple to compute the ratio between the pouring weight and the compression factor ψ (or L). Under the pressure of its own weight G , the powder, when poured into mold, has a relative volume β_0 , and under the pressure of a relative volume of 1. Figure 41 [in preceding text] shows that the leg of the right-angle triangle $\log \sigma_R - \log G$ equals the other leg $\beta_0 - 1$ multiplied by the tangent of the

angle formed with the x-axis, i.e. L:

$$L(\beta_0 - 1) = \log \sigma_R - \log G, \quad (23/1)$$

$$l(\beta_0 - 1) = \ln \sigma_R - \ln G, \quad (23/2)$$

For various powders of the same metal $\log \sigma_R - \log G$ is a constant, hence $L(\beta_0 - 1) = \text{const.}$ In most cases $l(\beta_0 - 1)$ equals 4 -- 7.

The dispersion and structural factors are reflected in the compression diagrams indirectly, determining the value of the volumetric characteristic of the powder. In those cases when powders of various dispersion had approximately the same volumetric characteristic, the author observed a very insignificant change in the maximum critical stress with the size of the particles.

Some detailed data on the effect of the volumetric characteristic upon powder compression was already discussed in paragraph 21.

24. The Compressing of Mixtures

The compressibility of charges made up of mixtures of powders of different metals as well as different powders of the same metal, is related to the volumetric characteristics of the initial powders and their mixture.

Generally speaking, there may be three cases of mixing powders with different pouring weights⁽²⁾. In the first case,

the volume of the mixture is subject to the rule of additivity, i.e. the volume of the mixture is equal to the sum of the volumes of the initial powders. If n_1 gravimetric parts of powder with a pouring weight γ_1 are mixed with n_2 gravimetric parts of powder with a pouring weight of γ_2 , the pouring weight of the mixture can be computed by formula:

$$\frac{n_1 + n_2}{\gamma} = \frac{n_1}{\gamma_1} + \frac{n_2}{\gamma_2} \quad (24/1)$$

whence

$$\gamma = \frac{(n_1 + n_2) \gamma_1 \gamma_2}{n_1 \gamma_2 + n_2 \gamma_1} \quad (24/2)$$

Most frequently the quantity of the poured mixture is somewhat in excess of what it should be by the rule of additivity, on rare occasions it is less.

If the pouring volume of the mixture responds to the rule of additivity, the volume of the mixture under pressure will be subject to the same rule.

If the pouring volume of the charge departs from additivity, the volume of the briquettes will also depart from additivity by the same degree.

Figure 46 is a compression diagram for a coarse electrolytic iron powder with a pouring volume of 0.47 cubic centimeters per gram, for a fine iron powder, obtained by reduction, with a pouring volume of 1.69 cubic centimeters per gram, and for the mixture of the two 50:50.

Logarithm of
specific pressure,
 $\log P, \text{ kg/sq cm}$

Relative volume β

Figure 46. Compressing a mixture of iron powders: 1. Pouring volume of 0.47 cubic centimeters per gram; 2. pouring volume of 1.69 cubic centimeters per gram; 3. the mixture of the two 50:50, computation by rule of additivity.

In mixing, the small particles located themselves between the large ones, causing thereby the pouring volume of the charge to depart from additivity. As per the rule of additivity, the pouring volume of the mixture is to be $\frac{0.47 + 1.69}{2} = 1.08$. The actual pouring volume is 0.88 cubic centimeters per gram, by 18 percent below the computed value.

The departure of the briquette volume from the computed value is approximately to the same degree. It can be seen that it takes a considerably lesser pressure to compress the mixture than it would follow from the rule of additivity (the logarithm of pressure in Figure 46 was reduced approximately by 0.3, which corresponds to a reduction in the pressure itself to half its value.

25. The Effect of Oxides

Oxides in powders are formed either on the surface of the particles as a result of oxidation in storage, or in some cases (when the powders are obtained by reduction) they are present

fully reduced iron powder No. 4 has an actual and computation porosity of 32.4 percent, the incompletely reduced iron powder No. 1 has an actual porosity of 48.2 percent and a computation porosity of 65.5 percent.

TABLE 25

Porosity of Iron Powders in Various Degrees of Reduction under the Pressure of 40 kg/sq mm

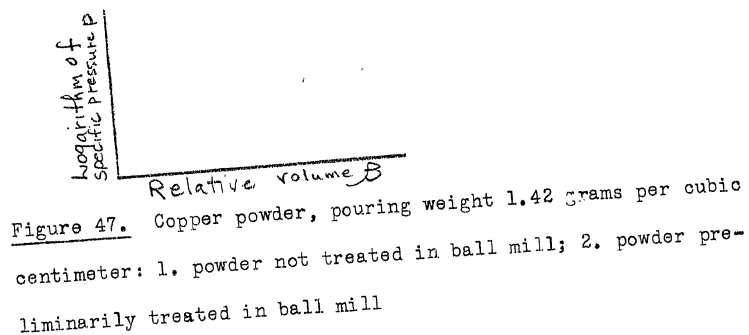
No. in sequence	Conditions of reduction		Degree of reduction (% of oxy- gen removal)	Pouring weight of powder, in gr/cu cm	Porosity	
	Tempera- ture in °C	Time in minutes			actual	compu- tation
1	600	30	51.7	0.22	48.2	65.5
2	700	10	51.7	0.24	38.0	58.7
3	700	30	58.9	0.21	39.6	57.4
4	700	60	100	0.18	32.3	32.3
5	800	10	76.1	0.23	36.8	48.5

The Effect of Preliminary Treatment on the Compressibility of Powders

In a number of cases, powders are subject to preliminary mechanical or heat-treatment. These treatments affect the compressibility of the powders to a considerable extent.

The treatment of powders in ball mills increases their pouring weight and the cold-hardening of the particles. The toughening of the particles increases the values of the critical stress σ_k and compression factor L at not too high densities

of the briquettes. It being the case that the values of specific pressure p , requisite for this degree of compressing reduction, are even reduced somewhat due to the increase in the pouring weight of the powder. Compressing to high densities greatly toughens the particles, hence, the initial cold-hardening effect of the preliminary treatment is not important in this case. Figure 47 is a graphic presentation of a typical case of compressing an electrolytic copper powder with a pouring weight of 1.42 grams per cubic centimeter prior to and after its treatment in a ball mill. The initial pressures, in the case of both powders, are somewhat different, but after attaining the value $\beta = 1.5$, the two curves in the graph blend into one. The cold-hardening sustained by the particles during the preliminary treatment of the powder has no effect upon the value of the critical stress σ_k (the pressure of extrusion).



In a number of cases, the method of obtaining the powder causes it to be brittle. Particles of such powders (for instance powders from gray iron chips) disintegrate easily in compression. Such brittleness reduces the toughness of the powders in compression, facilitating thereby their deformation. For instance, the brittle acicular chip of semisteel No. 19 (see Table 19),

under a pressure of 63 kilograms per square millimeter, has a porosity of 16.7 percent and a $\sigma_R = 130$ kilograms per square millimeter, while the less brittle chip No. 20, obtained through the light grinding of chip No. 19, has a porosity of 23 percent and a $\sigma_R = 200$ kilograms per square millimeter.

Preliminary annealing of the powders induces a change in properties and structure and has a substantial effect upon compressibility. Basically, the changes developed by annealing may be reduced to the following.

(1). A change in the volumetric characteristic. Low-temperature annealing reduces, while high-temperature annealing increases, the pouring weight of a powder. Therefore, if other changes induced by annealing are abstractly disregarded, it may be stated that a low-temperature preheating somewhat increases, while a high-temperature preheating somewhat reduces, the specific pressures, requisite for the obtaining of briquettes of not too high densities. In the case of high-density briquettes, the annealing of the powder, while changing the pouring weight, does not substantially affect the values of $\sigma_{R \max}$ and specific pressures.

(2). The removal of the cold-hardening effect. This factor reduces considerably the specific pressures p and the critical stresses σ_k in the case of briquettes of low density. The effect of this factor is reduced considerably with a high degree of consolidation, disappearing completely when a 100 percent density is attained.

(3). The diminution in the amount of admixtures (reduction of oxides in reduction annealing, the burning out of carbon in decarbonizing annealing, and the like). This factor reduces the values of p and σ_K (inclusive of $\sigma_{K \max}$).

In summing up the effect of the above factors, it may be taken that, in most cases, preliminary annealing considerably facilitates the operation in the press.

When dealing with alloy powders, two types of preliminary heat-treatment are to be differentiated.

(1). Heat-treatment to obtain solid solutions or intermetallic compounds from the initial metal powders. For instance, in heating copper-zinc charges, a brass powder is obtained. Since brass has a much higher hardness than the copper-zinc mixture, compressibility is decreased considerably at the expense of an increase in p and σ_K .

(2). Heat-treatment for dissociating solid solutions or intermetallic compounds into initial components. The graphitization annealing of the powders of white iron induces a disintegration of cementite into ferrite and graphite, it being the case that the hardness of the particles is reduced and the compressibility of the powder improved. For instance, the unannealed white iron powder No. 16 (see Table 19) has a value of $\sigma_K = 580$ kilograms per square millimeter, while after graphitization annealing, $\sigma_K = 150$ kilograms per square millimeter (powder No. 18, Table 19).

27. Other Formulations of the Ratio between Pressure and the Degree of Compressing Reduction

The semilogarithmic diagrams of compression make it possible to interpret the essence of the processes involved in the consolidation of powders. However, the values of the compression factor L change considerably even within small pressure intervals. It is, therefore, not always convenient to use the compression equation (19/10a):

$$\log p_{max} - \log p = L(\beta - 1)$$

It can be predicted a priori that the attempts to arrive at a compression equation with constant coefficients, to apply to all powders and to the entire range of pressures, is doomed to failure. Nevertheless, in a number of cases, it is possible to arrive at formulas with coefficients more or less constant within a wide range of pressures.

As brought out by the experiments conducted by the author, in the case of most of the powders of medium hardness (copper, iron), the compression factor L in the differential compression equation (19/6)

$$\frac{dp}{p} = l d\beta$$

can be presented as a function:

$$l = \frac{L}{0.434} = \frac{m}{\beta}, \quad (27/1)$$

where m is approximately constant within a rather considerable pressure range.

Then
$$\frac{dp}{p} = -l d\beta = -m \frac{d\beta}{\beta} \quad (27/2)$$

Integrating equation (27/2) for the interval in which m is a constant, we derive:

$$p\beta^m = \text{const.} \quad (27/3)$$

Here we have a ratio similar to the Boyle-Mariotte formula for gases, except that m does not equal 1.

The value of the constant in formula (27/3) can be derived by assuming $\beta=1$. Then p equals the maximum specific pressure $p_{\max}$ requisite for bringing the briquette to a fully compact state:

$$p_{\max} = \text{const.} \quad (27/4)$$

If the losses of pressure to friction against the walls of the press mold can be disregarded, then

$$p_{\max} = \sigma_{k\max},$$

where $\sigma_{k\max}$ is the maximum critical stress (the pressure of extrusion). In this case:

$$\sigma_{k\max} = \text{const.} \quad (27/5)$$

Conformantly with formula (27/1), when the relative volume $\beta=1$, the values of factor l and the compression exponent m are equal.

Since $\beta = \frac{1}{Q}$, where Q is the relative density of the briquette, equation (27/3) may be presented as:

$$\frac{p}{Q^m} = \text{const.} \quad (27/6)$$

value in metals of medium hardness, when toughened to a maximum degree, is approximately three times greater than in a non-cold-hardened state. The relative volume β is also diminished three times. Equation (27/2) can also be derived directly, if, in formula (19/2a), we assume a proportionality not between $\frac{dp}{A_H}$ and $\frac{dh}{h_0}$, but between $\frac{dp}{A_H}$ and $\frac{dh}{h}$.

Expressing equations (27/3) and (27/6) logarithmically, we obtain:

$$\log p + m \log \beta = \log p_{\max} = \log \sigma_{k \max} \quad (27/7)$$

$$\log p - m \log Q = \log p_{\max} = \log \sigma_{k \max} \quad (27/8)$$

In graphic presentation, equations (27/7) and (27/8) will be straight lines (Figure 48)

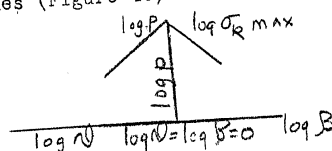


Figure 48. Ideal diagrams

$$\log \beta = \log p \text{ and } \log Q = \log p$$

The inclination of the straight line to the abscissa equals the compression exponent m , and the part, intersected by the straight line on the ordinate, equals the logarithm of the maximum specific compression pressure (in the ideal case, when there are no losses to friction in the press mold, it equals the logarithm of maximum critical stress).

Figure 49 is a presentation of logarithmic curves $\log p - \log \beta$ for certain powders. For most of the iron and copper powders, the curves are practically straight lines.

In the case of some other powders, they depart from rectilinearity. In this case, m is not a constant, and the values of m and σ_R at any point are determined, respectively, by the inclination of the tangent to the abscissa and by the point of intersection of the tangent with the y-axis.

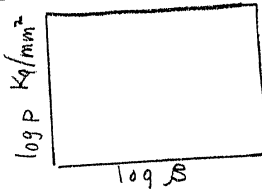


Figure 49. Logarithmic curve diagrams: 1. electrolytic tin, pouring weight 1.02 grams per cubic centimeter; 2. electrolytic copper, pouring weight 1.42 grams per cubic centimeter; 3. reduced tungsten, pouring weight 4.18 grams per cubic centimeter.

In the case of the semilogarithmic curve for electrolytic copper with a pouring weight of 1.42 grams per cubic centimeter (see Figure 42), the ultimate value of factor is greater than its initial value by 104 percent. The logarithmic curve for the same powder (Figure 49) shows a 10 percent difference between the ultimate and the initial values of exponent m . This example illustrates how much closer the logarithmic curves for metal powders of medium hardness are to rectilinearity. In the case of tungsten powders (see Figure 49) and copper MOZ, the initial values of exponent m are greater than the ultimate. In the case of tin powders, on the contrary, the ultimate values of m are greater than the initial. The values of m increase with the pouring weight of the powder and the hardness of the metal. The

σ_R values are determined by the hardness of the metal, and they approximately equal .

Table 26 is a compilation of the ultimate values of m and σ_R , computed by the logarithmic diagrams of some powders. For purposes of comparison with the data of Table 19, the σ_R - and L -values are given in terms of the semilogarithmic diagrams of these powders. As seen from Table 26, the σ_R -values for the logarithmic diagrams are closer to the pressure of extrusion (Table 20), in the case of all metals, except the very soft ones.

[See next page for Table 26]

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[See next page for Table 26]

TABLE 26

Values of m and σ_R Computed by Logarithmic Curve Diagrams

No. in sequence	Type of powder and its pouring weight in gr/cu cm	m	σ_R in kg/sq mm	Value of L and by diagram of curve		R E M A R K
				$\beta - \log p$	L in kg/mm ²	
1	Tin, electrolytic, 1.10	9.4	67	2.46	46	Sharp increase in m and from the den- sity of 72% (prior to this m 3.4 and 25 kg/sq mm
2	Tin, pulverized, 3.50	32.5	90	13.3	76	Sharp increase in m and from the den- sity of 78% (prior to this m 4.8 and 16 kg/sq mm
3	Copper, electro- lytic, 1.42	3.65	95	1.39	88	Curve approximates a straight line, in- itial values of m somewhat greater than ultimate
4	Copper, MOZ, 3.51	4.90	68	1.50	63	Initial m greater than ultimate
5	Iron, reduced, 0.67	2.7	118	0.9	98	Curve approximates straight line

TABLE 26 (Continued)

No in sequence	Type of powder and its pouring weight in gr/cu cm	m	σ_k in kg/sq mm	Value of L and by diagram of curve <i>B - log p</i>		R E M A R K
				L	in kg/mm ²	
6	Iron, electrolytic, 5.15 2.70	90	1.96	78		Same as above
7	Iron grit, 1.44	4.0	125	--	--	Same as above
8	Tungsten, 4.18	4.4	400	1.10	235	Initial values of m greater than ultimate

The Work of Compression

The pressure applied to the plunger of the press mold, in consolidating the charge, performs a certain amount of work. Let us evaluate this work by the following example. An iron powder with a pouring weight of 1.30 grams per cubic centimeter is being compressed in a press mold having a wide cross section. The height of the poured powder charge, non-compressed, is 6 millimeters. After being subjected to a pressure of 3000 kilograms per square centimeter, its height is reduced to 1.33 millimeters, which corresponds to a porosity of 25 percent (the height of the layer of compact material is 1 millimeter). Thus the path along which the work of deformation was performed equals $6 - 1.33 = 4.67$ millimeters. The work expended to accomplish the consolidation, is

$$\int_{h=1.33}^{h=6} P dh$$

where h is the height of the briquette,

P is the compression pressure,

which is some function of the height of the briquette

This work is made up of the following parts:

(1). Energy consumed in overcoming friction between the powder particles and the press mold walls. In this case, due to the small height of the powder layer, this fraction of the work may be disregarded. We shall see in Chapter V that friction, even when it consumes a considerable fraction of the energy expended, does not change the relationship between the work, the pressure, and the deformation, being reflected only in the value of the constants in the corresponding formula-

las.

(2). Energy consumed in the elastic deformation of the particles. Elastic deformation of the particles, with the height of the compact layer being 1 millimeter, a pressure of 3000 kilograms per square centimeter, and the elasticity modulus of iron 2×10^6 kilograms per square centimeter, may reduce the height of the briquette by 1.5 μ , which amounts to only 0.03 percent of the path traveled by the press mold plunger (of 4.67 millimeters). Thus, this part of the work is only a fraction of a percent of the entire energy consumed, and can, therefore, be disregarded.

(3). Energy consumed in the non-reversible "volumetric" deformation. In paragraph 17, it was mentioned that the powder particles, in compression, are flattened to a small degree only, hardly to the extent of 5 percent of their diameter. Thus, the pressure has performed the work of the non-reversible "volumetric" deformation of the particles not along the entire path (4.67 millimeters) of the plunger, but only along a section amounting to 0.05 millimeter. This fraction of the work approximately amounts to 1 percent, and may also be practically disregarded.

(4). Energy consumed in the surface deformation of the particles, i.e., in the displacement of the contact sections and in the formation of a new contact surface. This deformation occurs along the entire path (4.67 millimeters) of the plunger.

Hence, it may be assumed with a certain degree of precision that the work of compression is determined by the deformation of the contact surface in the displacement of particles into the pores, as per diagram in Figure 35 (preceding text), inasmuch as the other work components are practically insignificant.

Suppose, a powder with a reduced volume (see Paragraph 14) $V_k = 1$ cubic centimeter is being compressed in a press mold having a cross section of 1 square centimeter. The reduced height of the briquette $h_k = 1$ centimeter. The work of compression per unit of reduced volume, i.e., the reduced work w_k in the pressure interval from 0 to p , will be expressed by formula:

$$\int_{p=0}^p dw_k = - \int_{p=0}^p p dh = \int_{p=0}^p p d\beta \quad (28/1)$$

If the toughening effect is disregarded, then, in conformity with formula (19/6) $p d\beta = \frac{dp}{l}$, and, after making the corresponding substitution, we derive, after integrating equation (28/1):

$$w_k = \frac{p}{l} \quad (28/2)$$

With the toughening effect taken into account, after substituting into equation (28/1), in conformity with formulas (27/3) and (27/4), $\left(\frac{p_{max}}{p}\right)^{\frac{1}{m}}$, and again integrating equation (28/1), we derive:

$$w_k = \frac{p_{max}^{\frac{1}{m}}}{m-1} p^{1-\frac{1}{m}} \quad (28/3)$$

The maximum value for the reduced specific work at 100 percent-consolidation $w_{k \max}$ will be expressed by formula:

$$w_{k \max} = \frac{p_{\max}}{m-1} \quad (28/4)$$

Formula (28/3) can also be presented in the form:

$$\begin{aligned} w_k &= \frac{p_{\max}}{(m-1)\beta^{m-1}} = \frac{w_{k \max}}{\beta^{m-1}} = \frac{p\beta}{m-1} = \\ &= w_{k \max} \alpha^{m-1} = \frac{p}{(m-1)\alpha} \end{aligned} \quad (28/5)$$

If, in formulas (28/2), (28/3), (28/4) and (28/5), the magnitudes p and $p_{\max}$ are given in kilograms per square centimeter, the magnitude of the reduced specific work will be expressed in kilogram-centimeters per cubic centimeter, and if they are given in kilograms per square millimeter, the dimensionality of the reduced specific work will be expressed in kilogram-millimeters per cubic millimeter.

If work is expended for the consolidation of the powder only, and the losses to the friction of the powder against the press mold walls are disregarded, the magnitude of $p_{\max}$ in the above formulas can be substituted by $\sigma_{k \max}$, resulting in the formula below:

$$w_k = \frac{\sigma_{k \max}^{\frac{1}{m}}}{m-1} = p^{1-\frac{1}{m}} = \frac{\sigma_{k \max}}{(m-1)\beta^{m-1}} = \frac{\sigma_{k \max} \alpha^{m-1}}{(m-1)} \quad (28/6)$$

and

$$w_{k \max} = \frac{\sigma_{k \max}}{m-1} \quad (28/7)$$

It follows from formula (28/6) that the magnitude of the

specific work depends not only on the nature of the metal , but also on its volumetric characteristic (m). The reduced work increases with the hardness of the metal and with the diminution in the pouring weight of the powder.

The specific work of the consolidation w, i.e., the work of compressing the quantity of powder, which, under the given ultimate pressure and density, has a volume of 1 cubic centimeter, is linked to the reduced specific work w_k by formula:

$$W = w_k Q = \frac{w_k}{\beta}, \quad (28/8)$$

from which follows:

$$W = \frac{P}{m-1} \quad (28/9)$$

The work w of compressing a powder that has a reduced volume V_k cubic centimeters is linked to the reduced specific work by formula

$$W = V_k w_k \quad (28/10)$$

Footnote. Formulas (28/8), (28/9), and (28/10) prevail only in the case of absence of work losses to friction against the press mold walls.

As follows from formula (28/9), the compression exponent m is linked to the ratio between the specific pressure and the specific work by the following relationship:

$$m = 1 + \frac{P}{W} \quad (28/11)$$

The reduced specific work of compressing a powder may be computed by the compression diagram. With a small value of the reduced height of the briquette h_k , the formulas expressing the ratio between the work expended and the pressure and the density of the briquettes, coincide pretty accurately with the results obtained empirically in the case of most of the powders of iron and copper.

It follows from formulas (28/8) and (28/9) that the specific work of compression changes with the first power of pressure, and the reduced work of compression changes with pressure raised into a power of even less than unity. The work involved in the increasing of the contact surface of a compact body increases in a power greater than unity (Paragraphs 8 and 9).

29. Departures of Logarithmic Curves from Rectilinearity

If in equations $p\beta^m = P_{max}$, $m = m_1 = \text{constant}$ in the entire interval of densities, from $\beta =$ the relative volume of the non-consolidated powder to $\beta = 1$, then the compression diagram will be as presented in Figure 50, a.



Figure 50. Diagrams $\log p - \log \beta$: (a). the ideal curve;

(b). the real curve

In the interval between points A for the initial volume and B for $\beta = 1$, the curve runs along the straight line AB.

The tangent of the angle formed by line AB with the x-axis equals m_1 . When the pressure is diminished to a value below the weight of the powder, the relative volume will not expand to infinity, as it is algebraically required by formula $(27/3)$, but will remain without change. Hence, this point of the curve will be expressed by a vertical straight line $\log \beta = \log$ relative volume of non-consolidated powder (AA' in Figure 50,a). In this part of the curve $m = \infty$. When the pressure is increased above the P_{max} value, the volume, (if the relatively low compressibility of the compact metal is disregarded) will not change. Therefore, it can be assumed that, with the pressure above P_{max} , the curve will be expressed by the straight line $\log \beta = 0$ (BB' in Figure 50,a). For this part of the curve, too, $m = \infty$.

In reality, the curves run not along the broken straight line, as shown in Figure 50,a, but along a smooth curve of the type shown in Figure 50,b. In the case of all powders, without exception, magnitude m does not suddenly jump from infinity to the finite value m_1 , but is gradually diminished into it, within a predetermined interval of densities, which is dependent on the nature of the powder (Figure 50,b). By the same token, m passes from its finite value m_1 to infinity not in one jump, when $\beta = 1$, as in Figure 50,a, but, in most cases, gradually, as in Figure 50,b.

The reasons for the higher values of m at the beginning of compression may be basically reduced to the following:

- (1). In the very first stages of compression, deforma-

tion is sustained primarily by the surface layers of the particles containing admixtures that are harder than the basic metal (Paragraph 21).

(2). In a number of cases (such as when powders are obtained by mechanical disintegration), the surface layer of the particles has sustained a greater cold-hardening effect.

(3). A non-homogeneous distribution of density in the powder charge may at times cause higher pressures at the beginning of compression.

(4). The considerable part played by elastic deformations in the presence of the lowest pressures.

The higher values of m in the ultimate stages of compression are due to the following:

(1). In the ultimate stages of compression (see Paragraph 22), deformation is strongly inhibited by the cold-hardening, the growing toughness of the briquette, and geometrical factors.

(2). The density of the briquette is not uniform, and therefore, long before the 100-percent-compressing reduction is attained, part of the briquette has a density of 100 percent and develops as characterized by segment BB' (Figure 50,a), while another part changes as characterized by branch AB (Figure 50,a), with the resulting curve, characteristic for the entire briquette, running as indicated in Figure 50,b (also see Chapter VI).

At times, in the ultimate stages of consolidation, in the case of powders from soft metals and also under conditions of hot-pressing, the formula more conformant with reality, will be the one submitted by the author⁽²⁾, as follows:

$$\log p = n \sigma + C.$$

(29/1)

30. The Effect of Lubricants upon Compression Diagrams

The author conducted numerous experiments with the introduction into the pressing charge of all sorts of liquid and solid lubricants, such as oils, glycerin, stearin, paraffin, water, etc. In the case of a considerable reduced height h_k of the briquettes, the introduction of lubricants essentially reduced the external friction of the powders against the press mold walls (2 to 5 times), considerably reducing thereby the pressure requisite for the attainment of predetermined density. However, the nature of the compression curve, semilogarithmic and logarithmic, and the magnitudes of L and m, remained the same. In addition, the same reduction in pressure was effected by merely lubricating the press mold walls without introducing any lubricant into the pressing charge. In the case of low values of the reduced height h_k of the briquettes, the introduction of lubricant had no effect upon the compression diagrams, and the magnitudes p and σ_k did not change both under low as well as under high pressures.

The above results are of basic importance. They indicate that the compression pressure is determined not by forces required to overcome the internal friction between the particles

but by forces requisite for their deformation. Hence, the lubricants, while reducing the external friction of the powder against the inner surface of the press molds, had no effect whatever upon the internal friction. The recently published thesis by Sehlig and Wulff⁽¹³⁸⁾ confirms the fact that the introduction of lubricant into the pressing charge has approximately the same effect as the lubrication of the press mold walls.

That the compression pressure in its predominate part, is expended for the deformation of the metal, is already evident from the fact that the values of the critical stress σ_k , prevailing under any pressures and under any dispersion characteristics of the initial powders, conform to the hardness of the contact sections.

The author also experimented with the addition of water and other substances to nonmetallic powders. When these added substances were not reacting with the powder, no compression diagram changes were observed. For instance, with a low value of h_k , the addition of oil to the tungstic anhydride did not affect its compressibility. If, on the other hand, the added substance reacted with the powder (and each chemical reaction is unavoidably linked, at least, to the surface deformation of the particles), a very pronounced change in the compression curve was observed. Thus, the addition of water to the tungstic anhydride reduced the value of the pressure required for the attainment of the predetermined density several times as compared to dry powder.

The tungstic anhydride is a hydrophilic substance that enters into a reaction with water, the addition of which facilitates the deformation of the particles. Hence, additions affect compressibility only in the case when they react chemically with the particles of the powder facilitating thereby the deformation of the letter. The wet-pressing of ceramic materials is based upon this effect. Additions, which only reduce the coefficient of friction, but do not react with the powder, can only reduce the external friction in the press mold, but have no other effect upon the compressibility of the powders.

CHAPTER V

PRESSURE AND DENSITY DISTRIBUTION IN POWDERSLateral Pressure

In a briquette compressed to 100 percent-density and under a vertical pressure p_v , let us mentally conceive of a segregated cubelet (Figure 51) with 1-centimeter long ribs, parallel to the coordinate axes, it being the case that the z-axis is parallel to the pressure.



Figure 51. Diagram for the consumption of the lateral pressure

The pressure will cause the shrinkage of the cubelet in a vertical direction (z-axis) and expand it in a horizontal direction (x and y axes). The cubelet, however, being surrounded by a metallic mass, cannot expand, as a result of which lateral stresses p_r are evolved.

The transverse expansion in the direction of the x-axis is proportional to Poisson's ratio ν and the vertical pressure p_v , and inversely proportional to the elasticity modulus E , i.e., it equals $\nu \frac{p_v}{E}$.

The lateral pressure p_r , in the direction of the Y-axis, will also induce expansion along the X-axis, equal to $\nu \frac{p_r}{E}$.

Hence, the total expansion along the X-axis equals

At the same time, the lateral pressure p_r along the X-axis will induce shrinkage along the X-axis equal to $\frac{p_r}{E}$.

Since the lateral expansion of the cubelet is actually impossible, the total expansion along the X-axis must equal its shrinkage along the same axis, i.e.,

$$\nu \frac{p_v}{E} + \nu \frac{p_r}{E} + \frac{p_r}{E} = 0$$

from where

$$\frac{p_r}{p_v} = \bar{\epsilon} = \frac{\nu}{1-\nu}. \quad (31/1)$$

The same relationship can be deducted for the lateral pressure along the Y-axis.

The magnitude $\bar{\epsilon}$, i.e., the ratio of the specific lateral pressure p_r to the specific compression pressure, which, in the case of a compact briquette, equals $\frac{\nu}{1-\nu}$, is called the coefficient of lateral pressure.

The correlation between $\bar{\epsilon}$ and ν can also be expressed as follows:

$$\nu = \frac{\bar{\epsilon}}{1+\bar{\epsilon}} \quad (31/2)$$

Let us now pass to the value of the coefficient of lateral pressure $\bar{\epsilon}'$ and Poisson's ratio ν' for porous briquettes. Metallographic examination by the author (see Paragraph 17) indicated that the area of the microslide, occupied by the metal in a porous briquette, is in direct ratio to its relative density ν . Let us conceive of the relative density of the cubelet in Figure 51 as being equal to 60 percent, which would leave 40 percent of the lateral surface of separation ZY between

the cubelet and the metal surrounding it, for the pores. In this part of the surface, the cubelet can expand, and lateral forces are absent. Therefore, lateral pressure is evolved only at 60 percent of the surface of separation occupied by the metal, and equals only 60 percent of the lateral pressure which would exist in the case of a compact cubelet. It is the author's opinion that in the general case:

$$\epsilon' = \nu \epsilon, \quad (31/3)$$

where ϵ' is the coefficient of lateral pressure in a porous briquette;

ϵ is the coefficient of lateral pressure in a compact briquette;

ν is the relative density of the briquette (in fractions of unity)

Footnote. The actual lateral pressure may differ somewhat from the one computed by formula (31/3), since the relative density of the metal in a longitudinal direction may be somewhat higher, and in a transverse direction, somewhat lower than the general volumetric density .

The Poisson's ratio ν' of the porous briquette must be linked to the coefficient of lateral pressure ϵ' by the same correlationship as in the case of compact metal, i.e.,

$$\nu' = \frac{\epsilon'}{1 + \epsilon'} \quad (31/4)$$

from whence

$$\nu' = \frac{\nu \epsilon}{1 + \nu \epsilon} = \frac{\nu \nu}{1 - (1 - \nu) \nu}. \quad (31/5)$$

It follows from formula (31/3) that it can be substituted by formula (31/1) also in the case of porous briquettes if, instead of the nominal lateral surface, the reduced lateral surface of a porous briquette corresponds to $\mathcal{V}$ square centimeters of the reduced surface).

The values of ξ , ξ' and $\mathcal{V}'$ computed by the author with the aid of formulas (31/1), (31/3), and (31/4) for various briquette densities of certain metals, are compiled in Table 27.

[See next page for Table 27]

TABLE 27

Values of ν, ν', ξ, ξ' in Relation to the Metal and Density of the Briquette

	$\nu=100$ percent		$\nu=90$ percent		$\nu=80$ percent		$\nu=70$ percent		$\nu=60$ percent	
	ν	ξ	ν'	ξ'	ν'	ξ'	ν'	ξ'	ν'	ξ'
Tungsten	0.17	0.205	0.16	0.185	0.14	0.164	0.13	0.144	0.11	0.123
Iron	0.28	0.389	0.26	0.35	0.24	0.31	0.21	0.27	0.19	0.23
Tin	0.33	0.49	0.31	0.44	0.28	0.39	0.25	0.34	0.23	0.30
Copper	0.35	0.54	0.33	0.49	0.30	0.43	0.27	0.38	0.24	0.32
Gold	0.42	0.72	0.39	0.65	0.37	0.58	0.33	0.50	0.30	0.43
Lead	0.44	0.79	0.42	0.71	0.39	0.63	0.35	0.55	0.32	0.47

TABLE 27 (Continued)

	$Q=50$ percent		$Q=40$ percent		$Q=30$ percent		$Q=20$ percent		$Q=10$ percent	
	$\mathcal{V}'$	$\mathcal{E}'$	$\mathcal{V}'$	$\mathcal{E}'$	$\mathcal{V}'$	$\mathcal{E}'$	$\mathcal{V}'$	$\mathcal{E}'$	$\mathcal{V}'$	$\mathcal{E}'$
Tungsten	0.09	0.103	0.08	0.082	0.06	0.062	0.04	0.041	0.02	0.02
Iron	0.16	0.19	0.14	0.16	0.10	0.12	0.07	0.08	0.04	0.04
Tin	0.20	0.25	0.17	0.20	0.13	0.15	0.09	0.10	0.05	0.06
Copper	0.21	0.27	0.18	0.22	0.14	0.16	0.10	0.11	0.06	0.06
Gold	0.26	0.36	0.22	0.29	0.18	0.22	0.12	0.14	0.07	0.07
Lead	0.29	0.40	0.24	0.32	0.19	0.24	0.14	0.16	0.07	0.08

It follows from Table 27 that, with some exceptions, the values of ν and ϵ diminish with hardness and refractoriness of the metal. Poisson's ratio increases with the increase in the temperature of the metal, it being the case that the coefficient of lateral pressure, too, must increase.

Until now, no gauging of the lateral pressure in metal briquettes was attempted. American designers of press molds, according to the book by Wulff on "Powder Metallurgy" (155), assume the lateral pressure against the press mold walls to be 20 to 25 percent of the compression pressure. These figures are not far off from the data in Table 27. For instance, in the case of iron powders, at 30 percent-porosity, the coefficient of lateral pressure is 27 percent.

The formulas in this Paragraph are developed from the assumption of the impossibility of the lateral deformation of the press mold. In connection with the elastic deformation of the press mold walls, the actual lateral pressure may be below, but not above, the computed value. In the computations, it is also necessary to remember that the coefficient ϵ' is characteristic of the ratio of the lateral pressure not to the full compression pressure, but only to the part of the latter remaining after the deduction of losses to friction.

32. Loss of Pressure to Friction against the Press Mold Walls and the Pressure of Ejection

Let a briquette with a height h and a relative density ρ be in a cylindrical press mold of diameter D under a spe-

specific pressure of p (Figure 52). The total pressure upon the briquette $P = \pi D \frac{D}{4} p$.



Figure 52. Loss of pressure computation diagram

The pressure of 1 square centimeter of the lateral surface of the briquette p_r , according to formulas (31/1) and (31/3), providing the briquette is small, can be presented as $p_r = \xi' p$, where ξ' is the coefficient of lateral pressure for the relative briquette density of Q .

The entire lateral surface of the briquette equals πDh , and the total pressure upon it will be:

$$\begin{aligned} P_r &= \pi Dh p_r = \xi' \pi Dh p = \\ &= \xi Q \pi Dh p = \xi \pi Dh_k p, \end{aligned} \quad (32/1)$$

where ξ is the coefficient of lateral pressure with $Q = 100$ percent;

h_k is the reduced height of the briquette with $Q = 100$ percent

It follows from formula (32/1) that the total pressure upon the lateral surface of a briquette is equal to the product of the specific pressure by the reduced lateral surface of the briquette and by the coefficient for the lateral pressure of the compact metal. Thus, the total lateral pressure depends not on the compression pressure and not on the porosity of the briquette.

The loss of pressure to the friction of the powder against

the walls of the press mold ΔP , in conformity with formula (6/6) [in the preceding text], equals:

$$\Delta P = \mu P_r \quad (32/2)$$

where μ is the coefficient of friction of the powder against the press mold walls.

It follows from formulas (32/2) and (32/1) that:

$$\Delta P = \mu \xi \pi D h_r P. \quad (32/3)$$

The ratio between the loss of pressure ΔP and the total compression pressure P equals:

$$\frac{\Delta P}{P} = \frac{\Delta P}{\pi \frac{D^2}{4} P} = \frac{\mu \xi \pi D h_r P}{\pi \frac{D^2}{4} P} = \mu \xi \frac{4 h_r}{D}. \quad (32/4)$$

The loss of pressure to friction of the powder against the press mold walls may be determined with approximation experimentally, by proceeding from the following. Upon the discontinuation of pressure upon the briquette, the lateral pressure remains the same (P_r), since the walls of the press mold prevent the expansion of the briquette. Therefore, a force f must be used in order to eject the briquette.

This force

$$f = \mu P_r = \Delta P, \quad (32/5)$$

i.e., the pressure of ejection (maximum), f , is exactly equal to the loss in pressure ΔP .

Figure 53 is a graph diagram showing that such a correlation actually took place and that the pressure of ejection (equal to the loss of pressure) was always in direct

ratio to the compression pressure, regardless of the porosity of the briquette. Similar results were published in the thesis by Samoylov⁽⁵⁶⁾.

If after the diminution in the general pressure, the lateral pressure P_r is reduced to θP_r , where θ is the constant coefficient, which is less than unity in value, a proportionality shall be observed between the pressure of ejection f and the compression pressure.

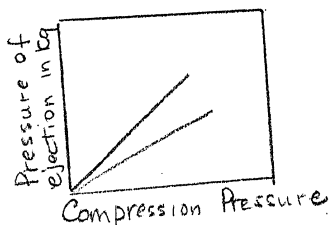


Figure 53. Ratio between the pressure of ejection and the compression pressure: $h_k = 20$ millimeters; $D = 13$ millimeters:
1. iron powder; 2. iron with 2 percent graphite

These experiments confirm the proportionality discussed in Paragraph 31 between the coefficient of lateral pressure ϵ' and the relative density of the briquette ρ .

The magnitude of the coefficient of friction μ in the case of dry metallic powders, without any special additions, fluctuated in the author's experiments from 0.08 to 0.20. Additions of graphite considerably reduced the loss of pressure and the pressure of ejection. For instance, the introduction into the pressing charge of 3 percent graphite reduced the coefficient of friction and pressure 2 to 5 times, and the introduction of 4 percent graphite, 3 to 6 times. The intro-

duction of various lubricants, such as stearic acid, oil, glycerin, reduced the pressure of ejection 1.5 to 5 times. In the author's experiments with the pressing of dry powders without any additions, the coefficient of friction was usually increased somewhat with the hardness of the metal.

Footnote. Dry lubrication (graphite) reduces μ without changing $\bar{\epsilon}$. Considerable quantities of liquid lubricant may, alongside of reducing the value of $\bar{\epsilon}'$, also increase the value of $\bar{\epsilon}$. This phenomenon may somewhat reduce the effectiveness of decreasing the pressures of ejection when liquid lubrication is used.

Formulas (32/1) and (32/4) prevail only when the values of h_k are insignificant. Indeed, formula (32/4) conforms precisely with what actually takes place only when the value of h_k is infinitesimal, i.e.:

$$\frac{dP}{P} = \mu \bar{\epsilon} \frac{4}{D} dh_k. \quad (32/6)$$

Integrating this equality, we derive:

$$\ln \frac{P}{P_h} = \ln P - \ln P_h = \mu \bar{\epsilon} \frac{4h_k}{D} = kh_k. \quad (32/7)$$

where P is the compression pressure at the plunger;
 P_h is the compression pressure at the bottom of the briquette, at the distance of h_k from the plunger;
 k is a constant. The pressure of ejection

$$p = P - P_h$$

and the ratio

$$\frac{p}{P} = \frac{P - P_h}{P} = 1 - \frac{P_h}{P}$$

The magnitude $1 - \frac{P_h}{P}$ approximates the value of $\ln \frac{P}{P_h}$ when ratio $\frac{P_h}{P}$ is close to unity. With an increase in h_k , i.e., when there is loss of pressure, $1 - \frac{P_h}{P}$ assumes a lower value than $\ln \frac{P}{P_h}$. Hence, it follows from formula (32/6) that, with the increase in the value of h_k , the losses of pressure and the pressure of ejection increase not in direct ratio to h_k , but less rapidly (particularly in the presence of high values of μ).

Some of the curves characterizing the ratio between the pressure of ejection (pressure losses) and the reduced height of the briquette h_k , as obtained by the author, are depicted in Figure 54. Prior to each pressing, the press mold was wiped with a "dry" cloth. The following conclusions can be drawn from these experiments:

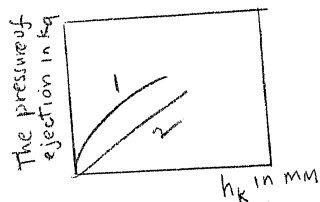


Figure 54. Ratio between pressure of ejection and h_k ,
 $D = 13$ millimeters; $P = 4000$ kilograms: 1. iron powder; 2.
 iron with 2 percent graphite

(1). When the value of μ is small (Figure 54, curve 2, iron-graphite), the pressures of ejection (losses of pressure) increase in direct ratio to h_k , in conformity with formula

$$\frac{p}{P} = \frac{P - P_h}{P} = 1 - \frac{P_h}{P}$$

The magnitude $1 - \frac{P_h}{P}$ approximates the value of $\ln \frac{P}{P_h}$ when ratio $\frac{P_h}{P}$ is close to unity. With an increase in h_k , i.e., when there is loss of pressure, $1 - \frac{P_h}{P}$ assumes a lower value than $\ln \frac{P}{P_h}$. Hence, it follows from formula (32/6) that, with the increase in the value of h_k , the losses of pressure and the pressure of ejection increase not in direct ratio to h_k , but less rapidly (particularly in the presence of high values of μ).

Some of the curves characterizing the ratio between the pressure of ejection (pressure losses) and the reduced height of the briquette h_k , as obtained by the author, are depicted in Figure 54. Prior to each pressing, the press mold was wiped with a "dry" cloth. The following conclusions can be drawn from these experiments:

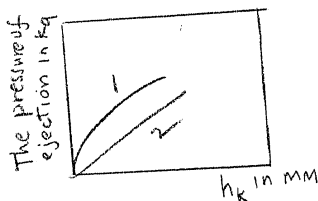


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(1). When the value of μ is small (Figure 54, curve 2, iron-graphite), the pressures of ejection (losses of pressure) increase in direct ratio to h_k , in conformity with formula

(32/4).

(2). When the values of $\frac{M^2}{D}$ are considerable (Figure 54, curve 1, iron powder), the increase in the pressure of ejection (losses of pressure) with the increase in h_k is slowed up, sometimes almost in conformity with formula (32/6), and frequently to an even greater degree than what is stipulated by this formula. Such departures from formula (32/6) are ascribed by the author to the non-homogeneous distribution of pressure and density along the cross section of the briquette (Paragraph 33).

It follows from formula (32/4) that the pressure of ejection (loss in pressure) varies in an inverse ratio to the value of the diameter D of the briquette. Actually, the pressure of ejection drops at a somewhat lower rate with the increase in diameter. This, too, is ascribed by the author to the non-uniform distribution of pressure and density along the cross section of the briquette (Paragraph 33).

33. Non-Uniform Density Along the Height and Cross Section of Briquettes

Loss of pressure to the friction of the powder against the press mold walls results in the non-uniform distribution of density both along the height as well as along the cross section of the briquette.

The drop of pressure with height is subject to formula (32/7).

$$\ln \frac{P}{P_h} = 4 \frac{\mu \xi}{D} h_k. \quad (32/7)$$

The expression $\frac{P}{P_h}$ can be substituted with approximation by $n \Delta Q$, where ΔQ is the drop in the relative density of the briquette at the height h_k from the plunger, n is the proportion factor (see formula (29/1)), which depends on the properties of the powder in the same direction as modulus L and the compression exponent m . We then derive:

$$\Delta Q = \frac{4\mu \xi}{nD} h_k = c h_k. \quad (33/1)$$

where c is a proportion factor that has a constant value within a certain interval.

Thus, the loss of density with height is in direct ratio to distance h_k (in reduced units) from the plunger.

Figure 55 is a graphic representation of the results of determination of density in various sections of cylindrical briquettes. To facilitate the division of the briquettes into separate parts by height, the powder was poured into the press mold by several batches separated by their interlayers of graphite^(2,54). The experiments showed that, in conformity with formula (33/1), the drop in density is in direct ratio to the distance h_k from the plunger, and is subject to the following rules:

- (1). The drop in density is diminished with the diminution in the value of the friction factor μ , i.e., with

the addition of graphite and lubricants (1.5 to 6 times).

(2). The drop in density with height is increased with the coefficient of lateral pressure $\bar{\epsilon}$.

(3). The drop in pressure with height is diminished with the diameter of the press mold.

(4). Double-end compression considerably improves the distribution of density.

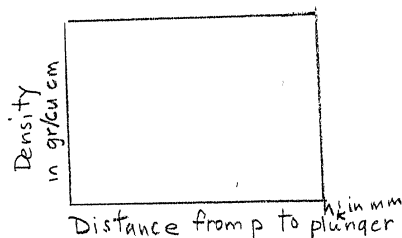


Figure 55. Variation in density along the height of briquettes:

1. copper, without graphite, single-end compression; 2. same, with 40 percent graphite; 3. copper, without graphite, double-end compression.

A vertical section of a cylindrical briquette compressed from a metal powder with interlayers of graphite is shown somewhat schematically in Figure 56. The cambered form of the [graphite-to-graphite] cylinder sections is due to the detaining effect of the press mold wall upon the movement of the particles. This flexure of the separate cylinder sections becomes greater with the height of the briquette and with the degree of consolidation. In Figure 37 [preceding text] showing the lamellar break in a copper ore concentrate slime molding, the camber of the layer can also be seen clearly. Figure

56 shows that in the upper section of the cylinder, nearest to the plunger, the maximum density will be at the edges, while in the lower section it will be in the middle. Figure 57 shows the distribution of hardness, as per Shor, in a compressed cubelet, which distribution also confirms the above.



Figure 56. The form of the sections of a compressed cylinder

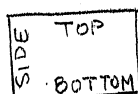


Figure 57. Distribution of hardness, as per Shor, in a compressed copper cubelet

The study of Figures 56 and 57 furnishes the answer to the question as to why the loss of pressure with height (Paragraph 32) may occur much slower than the rate implied in formula (32/6). In tall briquettes, the density near the walls of the press mold drops at a more rapid rate with distance from the plunger than it does inside the briquette. Hence, in tall briquettes, the pressure (vertical as well as lateral) is lower at the press mold walls than in the internal parts of the briquette. In low briquettes, density and pressure at the press mold walls may, on the contrary, be higher than in the internal parts. Therefore, the pressure of ejection, with an increase in the reduced height of the briquette h_k , will frequently increase at a lower rate than the rate implied in formula (32/6).

The non-uniform distribution of pressure and density cannot be explained to its fullest by the effect of the friction of the powder against the walls of the press mold. For

instance, in the complete absence of friction against the walls, the lateral pressure in the external parts of the briquette must be greater than in the internal parts. This effect increases with the width of the briquette. Hence, the pressure of ejection is diminished not in direct ratio to the briquette diameter, but at a somewhat slower pace (Paragraph 32).

34. The Effect of Briquette Dimensions upon the Compression

Diagrams

In Chapter IV we dealt with small briquettes, and we were in a position to disregard the pressure losses and the non-uniformities of density along height and cross section. In this case, the compression pressure was considered as the net pressure, which is used up exclusively for uniform consolidation. Hence, the $p_{\max}$ -value was equal to the critical stress σ_k .

In the case of large briquettes, there are present, on the one hand, losses of pressure to external friction, and, on the other hand, the non-uniform distribution of density, stipulated by internal friction, also induces a certain amount of excess pressure.

In the case of large briquettes, $p_{\max}$ is always greater than σ_k .

The briquette dimensions affect the compression diagrams in the following manner.

1. The effect of the briquette height

With the increase in the reduced height h_k , the losses of pressure to friction against the press mold walls are increased. In connection with this, the compression pressure is also increased. The increase in pressure with the increase in h_k can be expressed by the following formula (32/6):

$$\ln \frac{p_h}{p_n} = \frac{4\mu \xi}{D} h_k = kh_R, \quad (34/1)$$

where p_h is the pressure required for a predetermined degree of consolidation of a briquette with a reduced height h_k ; p_n is the net pressure required for the same degree of consolidation of a briquette with an infinitesimal height. It follows from formula (34/1) that the effect of the briquette height upon compression diagrams is expressed in the increase of pressure in a certain proportion (with the proportion factor the same at any degree of density). In the case of logarithmic and semilogarithmic curves the above effect must be manifested in the displacement of the curve ordinates by a segment proportional to h_k . The slope of the curves (and, consequently, the values of m and L) do not change as a result of this.

Figure 58 shows that such a displacement with some insignificant departures is actually observed. Such curve paths for briquettes with various heights also confirm the proportionality between the coefficient of lateral pressure ξ' and the relative density of the briquette Q (as established in Paragraph 31).

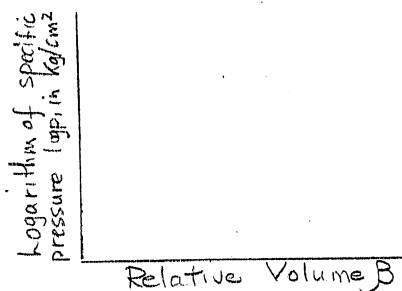


Figure 58. The effect of the compression height: 1. electrolytic copper, pouring weight 1.42 grams per cubic centimeter, $h_k = 0.6$ millimeters; 2. same, but $h_k = 4$ millimeters; 3. same, but $h_k = 8$ millimeters.

It is to be noted that maximum density, under the effect of a given pressure, occurs when compressing not the very smallest batches, but when compressing a briquette with some optimum reduced height value (Figures 58 and 59).

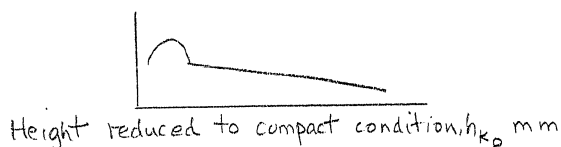


Figure 59. Density of tungsten briquettes in relation to briquette height, with p a constant.

The main cause for a reduction in the density of briquettes with a reduced height h_k below its optimum value is the excess pressure, stipulated by the non-uniform density of the charges with very small batches.

The data compiled in Table 28 confirm the above. A copper electrolytic powder was being compressed in a press mold, 15 millimeters in diameter. The optimum height h_k , in this case, was 2 millimeters. When h_k equalled 0.8 millimeter, the density was lower. As seen from Table 28, with a

small pressure ($p = 2.5$ kilograms per square millimeter), the difference in density was considerable (about 3 percent), with a considerable pressure ($p = 25$ kilograms per square millimeter), the difference was insignificant (0.1 percent).

Thus, in the first stages of compression, the effect of the non-uniformity of the charge was manifested strongly in the diminution of the density of the briquette with a low h_k -value. In the ultimate stages of compression this effect is less pronounced, since the losses of pressure to friction are smaller in the presence of small batches. Other powders, tested by the author, showed similar correlations.

TABLE 28

An Example of the Ratio between Relative Density and Pressure with Low Value of Reduced Height h_k (Electrolytic Copper Powder, Pouring Weight 1.50 Grams/Cubic Centimeter, Diameter of Press Mold 15 Millimeters)

Specific pressure p in kg/sq mm	Relative density ρ percent at	
	$h_k = 2$ millimeters	$h_k = 0.8$ millimeter
2.5	41.0	38.1
25	71.4	71.3

2. The effect of the briquette cross section area

With the increase in the diameter of the press mold, two contradictory factors affect the compression cycle. On the one hand, with the increase in the diameter of the end products,

the losses of pressure to external friction are reduced. These losses run in an inverse ratio to the diameter of the press mold (formula $(32/4)$). This factor leads to the diminution of pressures required for a given degree of compressing reduction, with an increase in the briquette diameter.

On the other hand, with the increase in the press mold diameter, the non-uniformity of the pressure and density distribution along the transverse section of the briquette is increased. This non-uniformity increases with the degree of consolidation, and it requires some "excess pressure". (Foot-note. It is simple to prove that the excess pressure is stipulated by the non-uniformity of density specifically along the transverse, and not longitudinal section). Hence, with the increase in the briquette diameter, the compression diagram factors L and exponents m increase, which may result in a diminution of briquette density in the presence of high degrees of compressing reduction (Figure 60).

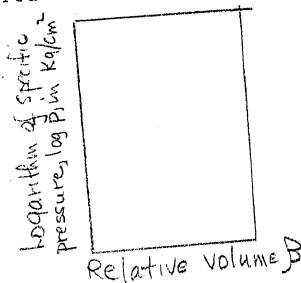


Figure 60. The effect of the press mold cross section (electrolytic copper, pouring weight 1.50 grams per cubic centimeter: 1. diameter of press mold equals 15 millimeters; 2. diameter of press mold equals 10 millimeters.

35. The Ratio between the Lateral Pressure and the Angle of Natural Repose in Non-Compressed Powders

Let a powder, poured into a box (Figure 61), sustain, under the effect of its own weight, a stress P_b . The powder will be transmitting to the walls a lateral pressure P_r , which equals $\epsilon' P_b$. If, under the effect of pressure, the left wall of the box should yield, the powder will begin to creep along an inclined plane, at an angle α to the vertical main pressure P_b .

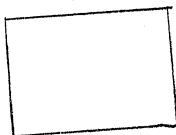


Figure 61. Diagram for computing the ratios between lateral pressure and the angle of natural repose

Let us analyze the stresses acting during the displacement [shear]. The stress normal to the plane of shear σ_n and tangent τ , as is known from the theses on "Resistance of Materials", can be presented by the main stresses P_b and P_r , as per the following formulas:

$$\begin{aligned}\sigma_n &= P_b \sin^2 \alpha + P_r \cos^2 \alpha \\ \tau &= (P_b - P_r) \sin \alpha \cos \alpha\end{aligned}$$

The resultant stress σ forms with σ_n angle φ , it

being the case:

$$\begin{aligned}\tan \varphi = \frac{\tau}{\sigma_n} &= \frac{(P_b - P_r) \sin \alpha \cos \alpha}{P_b \sin^2 \alpha + P_r \cos^2 \alpha} = \frac{(1 - \epsilon') \sin \alpha \cos \alpha}{\sin^2 \alpha + \epsilon' \cos^2 \alpha} \quad (35/1) \\ &= \frac{(1 - \epsilon') \tan \alpha}{\tan^2 \alpha + \epsilon'}\end{aligned}$$

Thus, the angle of the plane of creep α depends on the angle φ . It is known from textbooks on the mechanics of free-flowing bodies that the actual plane of creep will be a plane, where angle φ is at its maximum value, i.e., when

$$\frac{d(\tan \varphi)}{d(\tan \alpha)} = \frac{(1-\xi')(\xi' - \tan^2 \alpha)}{(\tan^2 \alpha + \xi') \cos^2 \varphi} = 0$$

This condition is satisfied when

$$\xi' - \tan^2 \alpha = 0$$

$$\tan \alpha = \sqrt{\xi'}. \quad (35/2)$$

Substituting in formula (35/1) $\tan$ by , we

derive:

$$\tan \varphi = \frac{\tau}{\sigma_n} = \frac{(1-\xi')\sqrt{\xi'}}{2\xi'} = \frac{1-\xi'}{2\sqrt{\xi'}} \quad (35/3)$$

Solving equation (35/3) for ξ' , we derive:

$$\xi' = \tan^2(45^\circ - \varphi/2) \quad (35/4)$$

In free-flowing bodies, the greatest possible pressure departure angle from the vertical equals the angle of friction, or, which is the same, the angle of natural repose φ . Hence, the value of the angle of natural repose φ is tied in with the coefficient of lateral pressure by formulas (35/3) and (35/4).

By formula (31/3)

$$\xi' = \eta \xi$$

where ξ is the coefficient of lateral pressure for compact material,

ρ is the relative density of the powder

Substituting in formulas (35/3) and (35/4) E' by ρE ,

we derive:

$$\tan \varphi = \frac{1 - \rho E}{2 \rho E} \quad (35/5)$$

and

$$\rho E = \tan^2 \left(45^\circ - \frac{\varphi}{2} \right) \quad (35/6)$$

Thus, the angle of natural repose (and, consequently, the coefficient of internal friction) is, for the powder of a given metal, a function of its volumetric characteristic.

For purposes of comparison, the angles of natural repose for copper powders of various pouring weights, both computed by formula (35/6) and established experimentally, are cited in Table 29. The coincidence of the empirical and theoretical figures is quite satisfactory, which is an additional confirmation of the proportional relationship between the coefficient of lateral pressure and the density of the powder.

[See next page for Table 29]

pected to increase the coefficient of lateral pressure ξ' and thereby decrease the angle of natural repose ϕ in the presence of a very great amount of liquid, $\xi' = 1$ and $\rho = 0$.

(4). Additions change somewhat the volumetric characteristic of the powder, which, in most cases, does not particularly affect the value of ϕ .

The author performed a series of tests in order to clarify the effect of various solid and liquid lubricants (graphite, oil, glycerin, paraffin, stearic acid) upon the angle of natural repose. The additions were introduced both by direct mixing as well as through volatile solvents in amounts up to 10 to 15 percent volumetrically.

Seemingly, the additions did not exert any perceptible gluing effect, since the fluidity of the powders (the amount of powder passing through a hole in a unit of time) was even increased.

The author did not discover any perceptible effect of the solid and liquid additions in the indicated quantities upon the angle of natural repose (and, consequently, upon the coefficient of internal friction). Yet, the same additions were reducing the coefficient of external friction of the powder against the press mold walls from two to six times.

In the presence of considerable amounts of liquid additions, let us say several times ten volumetric percent, the angle of natural repose was reduced considerably. This, how-

ever, is to be ascribed to the increase in the coefficient of lateral pressure ξ' , and not to the lubricating effect.

The results obtained by the author well agree with the available information relating to nonmetallic powders. For instance, in the Hutte manual, the following values for the angle of natural repose ϕ of free-flowing bodies, in the presence of various amounts of moisture, are cited (see Table 30).

TABLE 30

The Effect of Moisture upon the Angle of
Natural Repose (as per Hutte)

Free-flowing body	Pouring weight	ϕ	$\tan \phi$	$\tan^2(45^\circ - \frac{\phi}{2})$
	in gr/cu cm			
Earth, dry	1.4	35° - 40°	0.7-0.84	0.27-0.22
Earth, naturally moist	1.6	45°	1.00	0.17
Earth, water-saturated	1.8	27°	0.51	0.38
Sand, dry	1.58 - 1.65	30° - 35°	0.58-0.7	0.33-0.27
Sand, naturally moist	1.8	40°	0.84	0.22
Sand, Water-saturated	2.0	25°	0.47	0.41

In this case, the addition of water exerted a gluing effect, since the fluidity (friability) of moisture-containing earth and sand is diminished. Hence, in the presence of small

additions of water, the angle of natural repose is increased. Inversely, with high moisture content, the coefficient of lateral pressure ϵ' is increased, while ϕ is considerably diminished. Thus, the addition of water to nonmetallic free-flowing bodies exerts no lubricating effect.

Based on the above, the following deductions pertaining to the nature of the coefficient of internal friction can be drawn.

(1). The coefficient of internal friction is in sharp contradistinction both quantitatively and qualitatively from the coefficient of external friction. Thus, the coefficient of internal friction of copper powders (see Table 29, $\tan \phi$) had a value of 0.65 to 2.23, while the coefficient of external friction (see Paragraph 32) had a value of 0.1 to 0.2. Hence, the coefficient of internal friction is 3 to 15 times greater than the coefficient of external friction.

(2). Lubricating additions did not show any perceptible effect on the coefficient of internal friction of nonpressed powders. The same additions sharply reduced the coefficient of external friction (2 to 6 times). This result is to be juxtaposed with the data in Paragraph 30 (lubricating additions considerably reduced external friction and had no effect whatever on the "internal friction" in the briquettes).

(3). External friction is to a considerable extent stipulated by cohesions, therefore, lubrication will reduce its value considerably. In contradistinction to this, in order to overcome the so-called internal "friction", it is

necessary to deform the powder particles. Therefore, the introduction of lubricants will not perceptibly affect the coefficient of internal friction. The value of the coefficient of internal friction depends on the distribution of stresses in the free-flowing body, and is (completely) determined by the volumetric characteristic of the powder and the properties of the metal (formulas (35/4) and (35/5)).

Footnote. In connection with this, it is to be noted that the net pressure of compression is also fully determined by the properties of the metal and the volumetric characteristic of the powder.

CHAPTER VI

PHENOMENA TAKING PLACE UPON THE REMOVAL OF PRESSURE - THE

ELASTIC AFTEREFFECT

The Elastic Aftereffect

The processes taking place in the briquette after the pressure is taken off are very important and are frequently the direct cause of flaws resulting in rejections.

During the compression of the briquette, the external pressure, transmitted through the plunger, is counterbalanced by equal and oppositely directed internal elastic forces. The internal elastic forces develop not only in the direction of pressure, but in all other directions (lateral pressure), being counterbalanced by the reaction of the side walls of the press form.

When external pressure is removed, these internal elastic forces are freed, and, under their effect, the briquette tends to expand in all directions. The pressure in the direction of compression (longitudinal) is several times greater than in a transverse direction. Hence, the elastic aftereffect is more pronounced in a longitudinal direction.

With the external pressure removed, the transverse expansion is hindered by the side walls of the press mold, and longitudinal expansion -- by friction against the side walls. Hence, the effect of the internal stresses manifests itself mainly after the product has been ejected or taken out from

the mold. However, the aftereffect may to a certain extent be manifested also before the briquette has been removed from the press mold.

Figure 62 shows a typical curve graph for conditions of the powder under the pressure load and with load removed, as obtained on the Gagarin press (with subtracting the deformation of the press mold). The curve of unloading BA' descends vertically, since expansion is hindered by the detaining effect of the press mold walls. Sometimes, a little expansion occurs, and then the unloading curve will be the dotted BA''. With a repeat load, the pressure ascends to point B along the same branch A'B, and, with a further increase in pressure, along curve BC. If the pressing is done without intermediate unloading at point B, the variation in pressure and density will run along exactly the same type of load curve as ABC. Repeat load and unloading curves, due to the detaining effect of the press mold walls and to the inadequate sensitivity of the recording device, do not reflect the non-reversible variations occurring during repeat compressions. The fluctuations in electrical conductivity (Paragraph 37) are more sensitive, hence they register the non-reversible variations in multiple compressions (it being possible that some part, in this case, was due to the special design of the press mold for the purpose of measuring electrical conductivity).

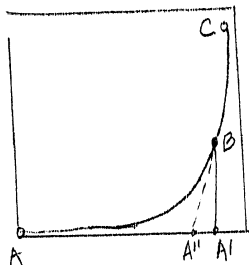


Figure 62. The loading and unloading curves in pressing

The elastic aftereffect must be taken into account in the design of the press mold. The easy removal of sleeves from internal rods, after the product is out of the press mold, is due to the elastic aftereffect.

It must be emphasized again that the elastic aftereffect induces not only a reversible elastic, but also a non-reversible deformation of briquettes. The elastic aftereffect absorbs (always only partly) the internal stresses. In conformity with the extent of this absorption, the "stressed" contact surface between the particles, resulting from compression, is reduced. The remaining unbroken contact surface -- the residual surface, is also "stressed", its size, in the opinion of the author, proportional to the value of the residual stresses. It is probable that the absorption of internal stresses occurs not by the way of a partial unloading, but by the way of a complete unloading, accompanied by the breaking apart in some sections and the complete retaining of stresses (equal to σ_R) in others. An approximate evaluation of the size of the residual contact surface is given in Chapter VII.

In a number of cases, the elastic aftereffect results in the breaking of the contact between particles along a considerable extent and the formation of the so-called lamellar fissures (see Chapter VII).

The extent of the expansion, induced by the elastic aftereffect, first of all depends on the interaction of two factors: the value of the elastic aftereffect and the toughness of the briquettes. If the bond between the particles is strong, the absorption of the internal stresses is insignificant, and expansion is little pronounced. When the bond between the particles lacks strength, the internal stresses are absorbed to a considerable degree, and expansion is great.

The minimum increases in size, following ejection, that were observed in the case of the best grades of industrial powders, were up to 0.5 percent in the direction of compression and 0.15 to 0.3 percent in a transverse direction. A simple computation shows that even such insignificant expansion is due not only to the elastic deformation of the particles, but also to their non-reversible shear. For instance, after a pressure $p = 4000$ kilograms per square centimeter, the expansion of an iron briquette (with a modulus of elasticity $E = 2 \times 10^6$ kilograms per square centimeter) in a longitudinal direction was 0.5 percent. Usually, in the presence of a 100 percent-absorption of internal stresses, elastic elongation should equal 0.18 percent, and the remaining 0.32 percent attributable to the shear of the particles of a different type with a diminution in the contact surface.

By the same token, the expansion in a transverse direction cannot be fully explained by the conventional elastic expansion of the briquette and the press mold, both induced by lateral pressures.

In low-grade powders, the longitudinal expansion attains a value of 5 percent, and the transverse expansion attains a value of 1 percent.

The author established the following basic regularities of expansion with the elastic aftereffect^(2,6).

(1) Expansion is increased under the effect of factors which reduce the strength of the bond between the particles of the briquette (see Table 31). The elastic aftereffect is increased with the diminution in the roughness of the particles and the increase in the pouring weight of the powder, with the increase in the amount of oxides and admixtures, in powders with flat particles, and the like.

(2). Expansion is increased with the hardness of the initial metal (see Table 31), since, with that, on the one hand, the importance of elastic deformation, as compared to plastic deformation, is increased (Paragraph 9, Tables 7 and 9), on the other hand, the toughness of the briquettes is diminished (Chapter VII).

(3). Expansion little depends on the pressure of compression. Although the internal elastic stresses increase in direct ratio to pressure, the toughness of the briquette is

increased to the same degree as pressure, and expansion remains unchanged. If the toughness of the briquette increases more rapidly, expansion is diminished with pressure; if the toughness increases at a slower rate, expansion is increased. Usually, the value of expansion is almost constant within a considerable range of pressures, increasing somewhat under the maximum and the minimum pressures.

(4). The greatest part of the expansion value develops immediately upon the ejection of briquettes. However, in a number of cases, some increase in dimensions may occur even after several days following the ejection from the press molds.

TABLE 31

Transverse Expansion after Ejection

Metal	Powder specifications	Relative	Expansion
		density of briquette, in %	along the diameter, in %
Copper	} Reduced powders with a relative density of the charge about 20%	65	0.25
Iron			0.27
Tungsten			0.48
Tin	} Granulated powders with a relative density of the charge about 45%	75	0.22
Copper			0.34
Iron			0.48

37. Changes in the Electrical Conductivity of Briquettes as a

Result of the Elastic Aftereffect

Skaupy and Kantorovich⁽¹⁴⁰⁾, also Kantorovich⁽¹¹³⁾ by himself, conducted a series of experiments with the compression of powders from tin, lead, gold, copper, silver, nickel, antimony, zinc, bismuth, tungsten, and graphite.

The measuring of electrical conductivity was conducted directly in the press mold. The compression pressure was parallel to the direction of the current. The plunger and the walls of the press mold were insulated from the powder by a layer of bakelite.

The above authors conducted repeat pressings without extracting the briquette from the press mold, with alternating loading and unloading, under pressures from zero to 2500 - 4000 kilograms per square centimeter -- up to 70 repeat cycles.

Kantorovich obtained the following results.

(1). In the first pressing, the electrical resistance R of the briquettes was reduced by pressure according to formula:

$$\frac{1}{R} = c\sqrt{P} + C \quad (37/1)$$

where P is the pressure, c and C are constants depending on the type of the material and conditions of the test.

(2). Resistance-pressure curves are non-reversible. In unloading, resistance at first retains its value attained in compression, and then, with the drop in pressure to low,

it increases rapidly. At times, the increase in resistance developed very slowly, and only a few days upon unloading it would rise sharply under the effect of a jarring. Under complete removal of pressure (but without ejection from the mold) resistance was increased several times. The growth of resistance with the removal of pressure is accelerated with the hardness of the powders. The drop in electrical conductivity with the removal of pressure is pronounced the strongest in the case of the hardest metal, tungsten. Electrical conductivity in this case dropped (with resistance increasing) approximately 10 times, and up to 50 times in individual cases.

(3). Under repeat pressures resistance was again dropping, yet, in the case of all powders tested (with the exception of tin, gold, one variety of lead, and, in some cases, graphite), it never attained its initial value. The increase in electrical resistance under repeat compressions was particularly clear in the case of hard metals. In tungsten, at the seventieth compression cycle, resistance under the pressure of 2000 kilograms per square centimeter was ten times greater than the initial resistance (see Table 32 below).

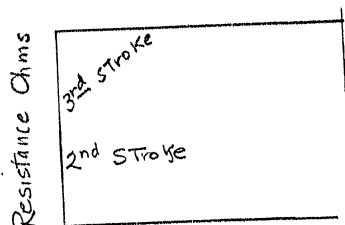
TABLE 32

Resistance (First Line) and Specific Resistance (Second Line)
of Tungsten Powder, as per Kantorovich

Pressure P in kg/sq cm	No. of cycle							
	1	10	20	30	40	50	60	70
0	0.753	0.149	0.193	0.198	0.303	0.408	0.519	0.663
	10.4	3.35	4.50	5.02	7.80	10.3	13.3	17.3
500	0.0348	0.0782	0.104	0.136	0.173	0.224	0.298	0.338
	0.64	1.88	2.60	3.30	4.43	5.74	6.75	8.92
1000	0.0234	0.0578	0.0784	0.0977	0.115	0.145	0.180	0.212
	0.48	1.41	2.03	2.54	3.20	4.03	5.4	6.06
1500	0.0179	0.0538	0.0688	0.0855	0.0975	0.121	0.140	0.160
	0.40	1.32	1.77	2.00	2.71	3.36	4.00	4.57
2000	0.0168	0.0447	0.0615	0.0770	0.0843	0.104	0.118	0.132
	0.42	1.18	1.68	2.11	2.37	3.0	3.58	4.20

(4). In repeat compressions, Kantorovich observed a phenomenon which he called inversion. The inversion (reverse stroke) was manifested by an increase in resistance with pressure (instead of a drop in resistance); see Figure 63. The inversion was observed by Kantorovich in the case of most of the powders (including one variety of gold), particularly in the case of the hard metal powders under repeat compressions. Soft metals

(tin) manifested no inversion.



Pressure, kg

(Scale plotted in direct ratio to the
square root of pressure)

Figure 63. The inversion observed in the compression of tungsten (as per Kantorovich)

The increase in resistance upon the removal of pressure and under repeat compressions were observed by Kantorovich both in the case of freshly reduced as well as oxidized tungsten.

Kantorovich and Skaupy ascribed the increase in resistance under repeat pressures by the considerable toughening of the hard metals under compression. The phenomena of inversion they left unexplained.

Jones (40) subjected their explanation to fair criticism. However, the theory which he himself advanced -- oxidation under repeat compressions, does not hold water.

Indeed, why should a pressure of 20 kilograms per square millimeter cause greater oxidation in tungsten than in softer and plastic metals? On the contrary, when taking into account the differences in hardness, this pressure should exert a much

greater effect in the soft metals than in tungsten. Then why would tungsten be subject to stronger oxidation? It is also not clear as to why oxidation should be manifested when pressure is removed and not when pressure is applied (see Table 31). Also, why does resistance sometimes rise sharply, as a result of a jarring, a few days after pressure has been removed? Could it be that with the jarring, a sudden oxidation occurs with lightning rapidity? Then, why is the path of the curves the same both in freshly reduced as well as in oxidized tungsten? And, finally, how can one explain, on the basis of the Jones thesis, the increase in the electrical resistance of graphite, which never forms hard oxides?

In addition, Jones ignored completely the phenomena of inversion.

Whereas, all the above observations by Kantorovich can be very simply accounted for by considering the elastic aftereffect.

The elastic aftereffect (see Paragraph 36) is particularly pronounced in the case of hard metals. In hard tungsten, after the removal of the pressure, the elastic aftereffect induced, breaks in the contact sections and mutual shifting of particles, as a result of which resistance was considerably increased. In the case of soft tin, the elastic aftereffect did not change the value of the interparticle contact surface, and resistance under repeat compressions practically does not change.

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Under conditions of repeat loading, in the case of hard metals, the pressure first of all induced a break in the already existing contacts and a mutual shifting of particles in accordance with the pattern presented in Figure 29,c in the preceding text. This, specifically, was the cause of the inversion observed by Kantorovich. Inversion should be pronounced the stronger the lower the toughness of the briquettes. We shall see in Chapter VII that the toughness of the briquettes decreases with the hardness of the metal. Hence, the inversion is particularly pronounced in tungsten and is completely absent in tin. With the further increase in pressure (Figure 65), the increase in the contact surface, according to the pattern in Figure 29,a, set in again, and the inversion was discontinued. However, due to the breaking of the preceding contacts during the inversion, the resistance could not drop again to the value attained in the preceding compression cycle, and, of course, resistance was increasing with each cycle.

An analogy can be made here with a tightly-packed suitcase. In disturbing the order of packing by rummaging through the suitcase, it may become impossible to close the lid tight even when greater pressure is applied. In some cases, such repeat compressions may promote the development of microscopic or even macroscopic fissures, which will increase resistance to an even greater degree.

38. The Effect of Air in the Briquette

Cracks and other types of flaws causing rejections in the pressing of bricks is ascribed by many ceramic specialists

to the detrimental effect of air bubbles entrapped in the pores of the material.

After the ejection from the mold, the expansion of the entrapped air causes a drop in density and the appearance of cracks in the product. In corroboration with this, the fact is cited that, when pressing in vacuum, briquettes of higher density and toughness, less subject to the development of fissures, are obtained. Let us quote the following from the thesis by Shapiro:

"Judging by American experience in the use of deaerated clay, the effect of air bubbles is to be considered as established specifically. In testing clay, slip in a hydraulic press, the compression pressure was raised to 600 kilograms per square centimeter, until characteristic fissures normal to the direction of compression appeared in the brick clay. When the air was thinned out in the mold to a relatively low degree of rarefaction, these fissures would disappear, appearing again only under higher compression pressure. A further rarefaction of the air in the mold permitted the use of still higher pressures before the reoccurrence of the above fissures. Hence, the fissures in the brick clay are due to the effect of the air present in the clay slip".

This experience gained in the field of ceramics was taken over [in toto] by some specialists in powder metallurgy, such as Hardy⁽⁹⁸⁾, Rostarchuk, and others. In some cases, the vacuum-pressing of metal powders⁽⁹⁸⁾ produces better results which seem to confirm the above.

It should be mentioned that the above specialists did not take into account the phenomena of elastic aftereffect, and fell into the error of explaining phenomena, due to the latter by the presence of air.

In the opinion of the author, such purely mechanical carry over of a concept from the field of ceramics into the field of powder metallurgy is wrong. Even when considering the presence of air (and not the elastic aftereffect) to be the basic cause of defects in the pressing of bricks, which will be shown below by the author to be not entirely so, it certainly is necessary to take into consideration the differences between the purely ceramic and the metalloceramic technological processes.

In ceramic technology, they use wet-pressing (even the so-called dry-pressing is essentially a "semiwet" process). The pressures employed are by tens and even hundreds of times lower than the pressures used in the consolidation of metal powders. Hence, the elastic aftereffect is relatively small. (Footnote. It must be added to the above that internal stresses in wet-pressing can be absorbed not only at the expense of the elastic aftereffect, but also as a result of molecular mobility. In this respect, the wet-pressing of ceramic masses is analagous to the hot-pressing process used in powder metallurgy). The gas-permeability of wet ceramic masses is negligible. Hence, the entrapment of air bubbles is really possible.

In the pressing of most of the coarse and medium metallic powders, with a particle diameter over 50 μ , air plays no

part whatever. The permeability of dry powder mixtures in this case is very great. For instance, the air-permeability of small pressed bushings, made from electrolytic iron powders with a particle size of 80μ , in the presence of an air pressure of $1/4$ atmosphere, amounted to 5 cubic centimeters per second, it being the case that all pores were capillary. It is obvious that, in the presence of such high permeability combined with the absence of closed pores, there can hardly be any mention of the entrapment of air bubbles in the pores. Nevertheless, such bushings showed tendencies to lamination.

The theory of air entrapment playing an important part in the development of fissures cannot survive a critical analysis from any other angle. Metal powders are usually compressed under a pressure of 4000 kilograms per square centimeter, with the volume of the pores reduced thereby 5 to 8 times. Hence, the entrapped air can hardly exert a pressure higher than 10 atmospheres. Such a pressure cannot constitute the cause for the development of fissures.

Whereas, the elastic aftereffect is immeasurably greater than the pressure of the entrapped air, specifically 400 times greater $\left(\frac{4000}{10}\right)$: Conformantly, the part played by the elastic aftereffect must be many times greater. With regard to the wet-pressing of ceramic materials, the correlation between the elastic aftereffect and the pressure of entrapped air is, as indicated above, an entirely different one. Hence, the direct actively-detrimental effect of the air is not great. But the indirect passively-detrimental effect of the air,

particularly in the pressing of fine powders, may be quite considerable. Fine powders have low permeability. Air in the presence of low permeability reduces the fluidity (friability) of powders. In vacuum, according to Hardy (98), friability is considerably higher (see Table 33 below).

TABLE 33

Amount of Powder in Grams Passing through a 3 Millimeter Hole
in One Minute

	36% fraction	65% fraction	95% fraction
Air Pressure	-325 mesh	-325 mesh	-325 mesh
Atmospheric			
760 mm of mercury column	382	110	0
Vacuum - 4 mm of mercury column	600	535	410

Poor friability results in non-uniform distribution of density and pressures in the briquette, on the one hand, creates additional excess pressure (Paragraph 34), and, on the other hand, it promotes the fissuring of the briquette during its ejection from the press mold. Thus, air may contribute (indirectly) to rejections. In this case, pressing in vacuum, by improving the friability of the powder, may promote the obtaining of articles with uniform distribution of density and pressures, that do not require any excess pressure and have a

lesser tendency to lamellar fissuring.

In the opinion of the author, even in the pressing of bricks, the direct cause of fissuring is the elastic after-effect. The entrapped air merely accelerates the effect of the latter, by hindering the obtaining of briquettes with a uniform distribution of density and internal stresses. The following considerations support the above opinion.

(1). In the pressing of bricks, the internal stresses, although not to such a degree as in the case of metallic powders, are considerably greater than the pressure of the entrapped air. In the above cited quotation from the thesis by Shapiro, it was indicated that the fissuring began under a pressure in excess of 600 kilograms per square centimeter. The pressure of the entrapped air was hardly in excess of 10 kilograms per square centimeter.

(2). The pressure of the entrapped air is in proportion to the decrease in porosity, i.e., it increases at a considerably slower rate than the compression pressure. For instance, when pressure is increased from 300 to 600 kilograms per square centimeter, the internal stresses are doubled, while the pressure of the entrapped air is increased to an insignificant extent only. Hence, were the entrapped air the direct cause of fissuring, the latter would set in at lower pressures than it actually takes place.

(3). According to Pascal's law, the pressure of the entrapped air is the same in all directions, and a haphazard

7

pattern of fissuring could have been expected. Actually, bricks show "characteristic fissures normal to the compression pressure", which can be easily explained as due to internal stresses, but cannot be explained by the effect of the air. In addition, the difference between the longitudinal and the transverse expansion in the briquette cannot be explained by the pressure of the entrapped air, but can be easily understood as a result of the elastic aftereffect.

CHAPTER VII

THE MECHANICAL PROPERTIES OF BRIQUETTES

39. Electrical Conductivity of Briquettes

The investigations by Kantorovich⁽¹¹³⁾ and by Skaupy and Kantorovich⁽¹⁴⁰⁾, relating to the electrical conductivity of compressed powders, were already utilized in Paragraph 37 for the understanding of phenomena occurring with the removal of the pressure.

The study of the electrical conductivity of briquettes helps with the answers to the following basic questions:

(1). How the processes of compression of powders run their course, how the powder particles are shifted and deformed, what takes place during that time with the surface admixtures, etc. A thorough understanding of the above is absolutely necessary in order to obtain materials of predetermined properties by controlling the procedure of the compressing reduction.

(2). What kind of a surface is the contact surface of the briquette particles and what is the character of the contact?

The study of electrical conductivity furnishes additional data pertaining to the manner in which the contact changes under compression, whether it is only at the expense of an increase in the contact surface, as per diagram in Figure 29,a, or is also due, to a considerable extent, to the shifting and break-

ing of the previous contact sections and the formation of new ones, as per type shown in Figure 29,c.

It was mentioned in Paragraph 37 that, during repeat compressions, Kantorovich observed the phenomenon of inversion, i.e., a higher electrical resistance of the briquettes with pressure instead of a lower resistance. This inversion may be understood only in the light of assuming a break in a considerable part of the previous contact sections and the formation of new ones, in accordance with diagram 29,c. Hence, there is no doubt that, during the repeat unloadings and loadings there occurs the shifting of particles with the breaking of the previous contact sections.

Kantorovich himself does not dwell on his thesis on the inversion during the first compression. However, in perusing his article⁽¹¹³⁾, the author discovered a case of inversion, which he overlooked. It was the specific resistance of tungsten briquettes under the increase of pressure from 1500 to 2000 kilograms per square centimeter that did not drop, but, on the contrary, showed an increase from 0.40 to 0.42 ohm-meter per square millimeter (Table 32, Paragraph 37). Under these conditions, there is no doubt that the shifting of particles with the breaking of contact, as per diagram in Figure 29,c, took place.

If, during the rapid compression of tungsten, the breaking of previous places of contact results in reduced electrical conductivity, then a time-lag under pressure, on the contrary, should induce a drop in electrical resistance. Table 34 shows

by the Kantorovich data, the effect of a time-lag under pressure upon the electrical resistance (the time-lag was effected in a screw press).

TABLE 34

The Drop in the Electrical Resistance of Tungsten Powder under Time-Lag Compression (as per Kantorovich)

			Resistance in ohms		
12 December 1928			13 December 1928		14 December 1928
from	-	to	from	-	to
0.113	-	0.006	0.008	-	0.005
					0.002
0.395	-	0.032	0.027	-	0.008
					0.009
0.860	-	0.108	0.095	-	0.029
					0.021

During a time-lag of three days, electro-conductivity increased 40 to 50 times. Such a high increase is, in all probability, due to a drop in the toughness of the insulating layer of admixtures in the places of contact between the particles during the prolonged time-lag, which increased the electrical conductivity of the briquettes.

Table 35 is a compilation of data by Kantorovich (113) and Trzebiatovskiy (151) showing by how many times the specific electrical resistance of metal powders exceeds that of the corresponding compact metals. The data by Kantorovich pertains to resistances measured in the press mold, prior to unloading, under a pressure of 25 kilograms per square millimeter. Trzebiatovskiy determined the resistance of the briquette after its ejection from the press mold (in this case, the electrical resistance was lowered by the elastic aftereffect).

The following conclusions can be drawn from Table 35:

(1). The electrical conductivity of briquettes is very low. It is, to a considerable extent, due to the oxides inhibiting the contact between the particles. Thus, under a pressure of 25 kilograms per square millimeter and a density of 56 percent, the electrical conductivity of copper is 90 times higher than that of the compact metal. In the case of graphite, under the same pressure and practically the same porosity (about 50 percent), it is only 2.2 times higher. Such a considerable difference is due to the presence of oxides in copper and their absence in graphite.

(a). The purely metallic surface of contact in pressed powders is usually very small. In conformance with the data in Paragraphs 4 and 7, the contact surface of a single layer (contact cross section) A should change as per equation (A in direct ratio to p):

$$\lambda = \frac{1}{p} = k A^{\frac{1}{2} + \frac{1}{n}}, \quad (39/4)$$

whence

$$\frac{\lambda}{k} < A < \left(\frac{\lambda}{k} \right)^2, \quad (39/5)$$

where λ is the specific electrical conductivity

p is the specific resistance of the briquette,

k is the proportion coefficient

n is greater than 2

A is the metal contact surface of a single layer

It follows from this that the surface of the purely metallic contact in a single layer of a copper powder, under a pressure of

Table 35

The Electrical Resistance of Compressed Powders

<u>Metal of the powder</u>	<u>Pressure in kg/sq mm</u>	<u>relative density of powder in %</u>	<u>Ratio between the resistance of a compressed powder and the compact metal</u>	<u>Source of data</u>	<u>Remark</u>
Tin	25	95	1.1	Kantorovich	Resistance under pressure of 25 kg/sq mm prior to un- loading
Lead	25	100-84	1.7 - 3.0	"	"
Graphite	25	50	2.2	"	"
Zinc	25	89	2.6	"	"
Gold	25	49-63	7.5 - 12.0	"	"
Bismuth	25	84	7.9	"	"
Antimony	25	76	14 - 29	"	"
Silver	25	85-81	31 - 69	"	"
Copper	25	56	90	"	"
Platinum	25	32	100	"	"
Nickel, hard	25	63	120 - 150	"	"
Nickel, soft	25	76-81	18 - 26	"	"
Iron	25	51	185	"	"
Tungsten	25	73	114 - 420	"	"
Gold	150	about 95	1.7	Trzebiatovskiy	Resistance after ejection from press mold
Copper	150	about 95	216	"	"

25 kilograms per square millimeter, occupies less than 1 percent of the cross section of the briquette. Upon ejection from the press mold, the elastic aftereffect will further reduce this fraction.

(3). With the increase in pressure and density, the effect of oxides upon the specific electrical conductivity is diminished. For instance, in the case of a tin powder, for which a specific pressure of 25 kilograms per square millimeter is considerably in excess of the critical stress σ_R , electrical resistance is only somewhat greater than in the case of the compact metal.

Under the pressure of 150 kilograms per square millimeter, the specific resistance of a copper briquette (additionally increased by the elastic aftereffect upon ejection from the press mold) is only 2.6 times higher than in the case of the compact metal.

The diminution of the effect of oxides under high pressures may be explained in part by the considerations submitted in Paragraph 4, but, in addition to that, the stripping of the oxide layer may occur under compression.

40. The Porosity of Briquettes

All the properties of the briquettes -- mechanical, electrical, thermal conduction, behavior in baking, etc., are linked directly or indirectly to their porosity. Porosity is most significantly and directly reflected in the permeability of briquettes with relation to various liquids and gases and

in their ability to absorb liquids, for instance, oil. For a complete characteristic of porosity, it is necessary to know not only the total volume of all pores, but also the magnitude and disposition of individual pores, the percentage of open and closed pores, and the permeability of the briquette in various directions.

Permeability depends to a much greater degree upon the size of the individual pores than upon the total volume of all pores. For instance, the permeability of a briquette with a porosity of 20 percent, compressed from powder particles 100 μ in size, is greater than the permeability of a briquette with a porosity of 40 percent, but with a particle size of 10 μ . It was pointed out in Paragraph 12 (Table 10) that the permeability of powders with a uniform size of particles, in the presence of the same degree of porosity, is increased in direct ratio to the square of the diameter of the particles, or, which is the same, to the square of the diameter of the pores (or to the cross section area of the pores in the first powder). When the particles are not uniform in size, there are difficulties in determining the mean "effective" diameter of the pores. The smaller particles are usually distributed in the intervals between the larger ones, thereby reducing considerably the cross section area of individual pores. Therefore, the mean "effective" diameter of the pores is determined to a greater degree by the fine fractions of the powder.

Permeability depends on the total porosity (and, consequently on the compression pressure) in a very complex manner.

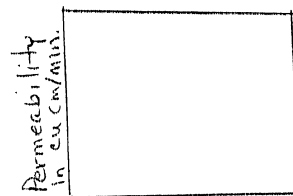
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If, in the presence of a reduction in total porosity n times, the size of each pore will also be reduced n times, permeability will be reduced n^2 times.

Such a ratio is very frequently observed in reality (see curve 1, Figure 64). However, sometimes under pressure, the first to be compressed are the largest and the most permeable pores, and, in these cases, permeability changes more rapidly than with the square of porosity. Under certain compression pressures (or, which is the same, at certain porosities), conglomerations of particles or the particles themselves may become pulverized. The magnitude of the pores, under such conditions, is reduced abruptly, together with an abrupt reduction in permeability. For instance, the author observed when compressing pieces of baked iron grit with 1 millimeter sized conglomerates and particles of 30μ in size under pressures that were breaking up the conglomerates into separate particles (curve 2, Figure 64). In other cases, the first to be reduced under compression are the nonpermeable intraparticle pores, and then permeability changes less rapidly than with the square of porosity, sometimes even in proportion to the first or even a fractional power of porosity. In very rare cases, even an increase in permeability was observed in the presence of a reduction in porosity (curve 3, Figure 64). This phenomenon is due to the formation of lamellar fissures under high compression pressures (see Paragraph 48).



Porosity

Figure 64. Permeability of briquettes: 1. iron, reduced, minus 80 mesh; 2. iron grit, 1 millimeter; iron, electrolytic, minus 80 mesh

Porosity, as all the other properties of the briquettes, is anisotropic, and it depends on the direction of the compression pressure. In longitudinal section (parallel to the pressure), both total porosity, as well as the size of the individual pores is less than in transverse section (see Figure 38 in preceding text). Therefore, permeability in a longitudinal direction (when a gas or a liquid moves through the transverse cross section of the pores) is usually greater than in a transverse direction (when a gas or a liquid moves through the longitudinal cross section of the pores). The actual gauging of the porosity of metal briquettes in various directions was not, as yet, attempted. Nevertheless, the correctness of the above consideration is confirmed by the data of Professor Savarenskiy⁽⁴⁹⁾ pertaining to the permeability of soils (the particles of which are orientated under the pressure of the weight of the soil itself) in various directions (Table 36). As will be seen from the Table below, permeability of the soil in a vertical direction (the direction of the force of gravity) is considerably greater than in a horizontal direction.

TABLE 36

Variation in the Permeability of Soils in Various Directions
of Water Filtration (as per F. Savarenskiy)

Type of soil	Coefficient of filtration in m/24 hours with the water moving		Ratio of permeability in a vertical direc- tion to permeability in a horizontal di- rection
	in a horizon- dir direction	in a vertical direction	
Loess sub-argil- laceous	0.310	12.21	37.5
Same as above	0.017	0.12	7.0
Same, water- bearing	0.378	1.72	4.5
Same as above	0.011	0.11	10.0

During the ejection of the briquette from the press mold, transverse lamellar fissures may occur at times, resulting in greater permeability in the transverse direction than in the longitudinal.

In most cases, industrial powders have very insignificant intraparticle porosity, and, therefore, the percentage of closed pores in the briquettes, as indicated by measuring the capacity for absorption, equals zero.

41. Primary Data on Mechanical Properties of Briquettes

Figure 65 shows a typical compression curve for a copper powder briquette. The deformation values (changes Δl in the initial length l of the pressing charge) are plotted on the abscissa, and the deformation loads P are plotted on the ordinate.

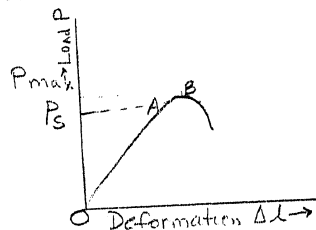


Figure 65. Compression curve of briquette

As seen from Figure 65, the deformation diagram of the metal powder briquette is qualitatively no different from the deformation diagram of the compact metal. As in the case of compact metals, there is a rectilinear (or almost rectilinear) curve segment OA. If at point OA the load is removed from the specimen, the curve of unloading will coincide with the curve of loading. Thus, in this interval, the load induces a "reversible" deformation. Beyond the limits of the rectilinear segment, the curve is non-reversible, and the load induces residual deformation.

Hence, similarly to the modulus of elasticity of compact metal, we can speak of the modulus of "elastic" or "reversible" compression. It is obvious that the modulus of compression of briquettes E' , within the limits of the reversible segment of the curve can be expressed by formula

$$E' = \frac{P}{f} : \frac{\Delta l}{l} = \frac{P}{\Delta l} \cdot \frac{l}{f}, \quad (41/1)$$

where P is the load (normal pressure);

f is the nominal area of the initial cross section of the briquette;

l is the initial length (height) of the briquette;

Δl is the reduction in length under load.

In differential form, the modulus will be expressed by formula

$$E' = \frac{dp}{dl} \cdot \frac{l}{f}. \quad (41/2)$$

By the same token, we can introduce (in keeping with the conventional terminology of the testing of metals) the concepts of proportional limit, elasticity, and yield of briquettes. For instance, the conditional yield point σ_s of the briquette may be considered as the load pertaining to the initial area of its transverse cross section $\frac{P_s}{f}$, at which the deformation curve departs from rectilinearity by 0.2 percent of its initial length, i.e.,

$$\sigma_s = \frac{P_s}{f}.$$

The ultimate compressive strength (or by the old terminology, temporary resistance to compression) corresponds to the maximum load $P_{\max}$ pertaining to the initial cross section of the briquette (see Figure 65):

By the same token, the terms determining residual deformation under the effect of load (compression, elongation, deformation of transverse cross section), are similar to the conventional terminology in the testing of materials.

The qualitative analogy between metal powder briquettes and compact metals is not limited to the deformation diagrams only. For instance, in compact metals, when the load passes beyond the yield point of the metal, there appear lines of creep, the so-called Luders lines, inclined at an angle , somewhat less than 45 degrees, to the direction of compression. By the same token, during the compression of powders, soon upon the passing of the yield point, lines of "creep", similar to the Luders lines, sometimes up to several times ten millimeters long, appear (see Figure 66, a and b) below. Under microscopic examination, it can be discerned that these lines pass through the pores and fissures (as different from the compact metals, where these lines pass through the grains).



Figure 66. Lines of "creep" in briquettes: a. diagram; b. microphoto, x by 40

The disintegration of briquettes under compression is in many cases similar to the disintegration of compact metals, (see Figure 80, further down). But, although there is some (incomplete) qualitative similarity between briquettes and

compact metals, the considerable qualitative differences between them must not be lost sight of. For instance, the angle α between the lines of "breep" and the direction of compression departs to a greater extent from 45 degrees in the case of briquettes than it does in the case of compact metal. In briquettes, conformantly with formulas (35/2) and (35/4),

$$\tan \alpha = \sqrt{E'} = \tan (45^\circ - \varphi/2)$$

where E' is the coefficient of transmission of lateral pressure;

φ is the angle of internal friction

In conformity with Table 27 (Paragraph 31), $\tan \alpha$, in the case of copper powder briquettes at 40 percent porosity, should equal 0.57. Actually, it is even less (about 0.45).

Footnote. These departures from the computation data are due to the difference in porosity in various directions under compression with the possibility for lateral expansion present (in contradistinction to compression with the possibility for lateral expansion absent). In this case, the pores between the horizontal rows of particles are diminished, while between the vertical rows they are, on the contrary, increased. Hence, the coefficient of lateral pressure E' should be lower in value than in Table 27, while the angle of internal friction φ , on the contrary, should be greater.

42. The Modulus of Elasticity of Powder Metal Briquettes

Footnote. It must be remembered that all the formulas in this Paragraph are satisfied only when "net" pressures are used (see Paragraph 35). In the case of two briquettes compressed from the same powder under various "gross", but under the same "net" pressures, the moduli are approximately the same.

Figure 67 below is a graphic representation of the ratio between the modulus of "elastic" compression of some metal powders and the compression pressure.

(Footnote. In the book by the author "Metalloceramics"⁽²⁾ there are certain errata in the text pertaining to the moduli of briquettes). The moduli were measured in a Gagarin press and in a TsNIITMASH IM4a machine (with corresponding allowances for the deformation of the testing machine itself).

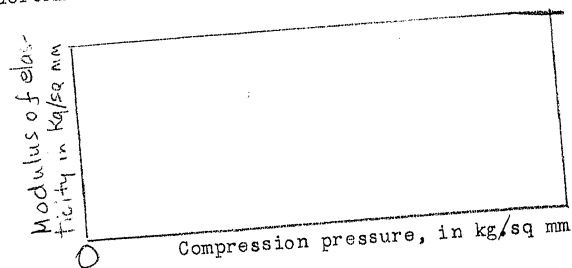


Figure 67. Ratio between the modulus of elastic compression and the compression pressure (iron, reduced from slag)

The following basic deductions can be made from these experiments.

- (1). The moduli are approximately in direct ratio to

the specific compression pressures (Footnote. This ratio was first established by Tertsagi on soils).

(2). The moduli of briquettes are considerably lower in value than the moduli of the corresponding compact metals. For instance, in the case of copper and iron powders, under net pressures of about 10 kilograms per square millimeter, they are 20 to 100 times lower in value than in the case of the corresponding compact metals.

(3). The value of the moduli of briquettes, in a number of cases, does not depend on the value of the moduli of the corresponding compact metals. For instance, the modulus of iron powders was at times somewhat below the modulus of copper powders (with the same compression pressures). At the same time, the contrary is true of the compact metals (the modulus of copper is 2.5 times below the modulus of iron).

(4). The moduli of compression in the direction of compression pressure are usually somewhat higher than the moduli of compression in a transverse direction.

Thus, in contradistinction to the moduli of elasticity of compact metals, the values of which practically do not depend on structure and cold-hardening, the moduli of metal powder briquettes are a function of the residual stresses localized in the contact sections of the particles (these stresses are in direct ratio to the compression pressure).

Therefore,

(42/1)

$$E' = K \theta P,$$

where E' is the modulus of "elasticity";

θ is a constant coefficient, less than unity, characterizing the fraction of the residual stresses (of the residual contact surface) with relation to the stresses (contact surface) under compression;

p is compression pressure;

θp expresses the residual stresses in the briquette;

k is the proportion coefficient between the modulus and the residual pressures.

The modulus of the briquettes (as also all their other properties) is rather a contact interparticle than an intraparticle property.

The diagram below explains the correlationship between the modulus of "elastic" compression pressure (Figure 68).

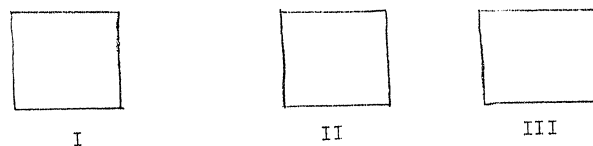


Figure 68. Diagram explaining the correlationship between the moduli and compression pressure

Let the copper bodies (particles) A, B, and C be pressed against each other by pressure p' , which is analogous to the residual stresses in the briquette (see Figure 68). If we apply to particle B a certain force p'' (analogous to the external load during the deformation of the briquette), particle B, acting as a lever, lifts particle A to some height (Figure

68, II). This displacement of particle A is analogous to the deformation of the briquette. It is obvious that, if we increase force p' twice, it will be necessary, in order to obtain the same deformation (displacement) of the system, also to increase force p'' twice. Hence, the modulus of the system (ratio of load p'' to the displacement of particle A) is in direct proportion to the value of the residual stresses p' . If pressure p' is discontinued, particles of A, B, and C will revert to the previous position (Figure 68,I), provided that p'' did not exceed some predetermined value (this value of p'' corresponds to the proportional limit of the briquette). Thus, the deformation of the system will be a "reversible" one. The conditional characteristic of this "elasticity" must be remembered, however, since the contact places of particles A, B, and C, after unloading will be somewhat displaced (as, for instance, the contact between the earth, the lump, and the crowbar after the pressure upon the crowbar is discontinued). If the value of force p'' will exceed a certain predetermined limit, particle A may be thrown off particle C (Figure 68, III). This disposition corresponds to non-reversible deformation after the proportional limit has been exceeded.

The displacement of particles A, B, and C, under conditions of adequate hardness of the material, depends on their mutual disposition and on pressure p' , and not on the modulus of the material itself. Therefore, if the copper in particles A, B, and C is replaced with iron, the displacement of particle A under load p'' and the modulus of the system will not change

substantially. This clears the point as to why, in a number of cases, the modulus of the briquettes does not depend on the modulus of the corresponding metal.

The modulus of elasticity can be contemplated also from another viewpoint. To a briquette with a nominal cross section that equals unity, and is compressed under pressure p , let there be applied in a longitudinal direction an external load G . The residual surface of the "contact" cross section of this briquette is determined by formula (see Paragraph 16):

$$A'_H = \theta \frac{p}{\sigma_R} \quad (42/2)$$

where p is the compression pressure;

σ_R is the critical stress;

θ is the constant coefficient, less than unity, characterizing the fraction of the contact cross section (or, which is the same, the fraction of internal stresses) remaining after ejection from the press mold.

It may be assumed that, if the external load G is less than the residual stresses θp , the proportional limit will not be exceeded, and the residual contact surface $\theta \frac{p}{\sigma_R}$ will practically not change. In this case, load G (see Paragraph 16) is to be considered as applied not to the entire nominal cross section, but to the residual contact cross section, as determined by formula (42/2). Hence, the elastic relative deformation under compression will be not $\frac{G}{E}$, but $\frac{G \sigma_R}{\theta p E}$. Thus, it is not the value E of the modulus of the compact metal that may be accepted as the modulus of

elasticity [of the briquette], but a smaller value E' , which is determined by formula

$$E' = \frac{\theta E}{\sigma_k} p = k p, \quad (42/3)$$

it being the case that k , the proportion coefficient, equal to $\frac{\theta E}{\sigma_k}$, has a constant value, provided the phenomena of cold-hardening are disregarded.

In the case of iron briquettes, for instance, where $\theta = 0.5$, $E = 20,000$ kilograms per square millimeter, and $\sigma_k = 100$ kilograms per square millimeter, the modulus of elasticity equals $100p$, and, with $\theta = 0.1$, it is equal to $20p$. In the case of copper briquettes, with $E = 8000$ kilograms per square millimeter, $\sigma_k = 80$ kilograms per square millimeter, and $\theta = 0.9$, the modulus equals $90p$. In the case of hard metals (see Paragraph 9, Table 9), the values of both θ as well as the ratio $\frac{E}{\sigma_k}$ are less than in the case of soft metals (Foot-note). There are some exceptions, for instance, in iron $\frac{E}{\sigma_k}$, but not θ , is higher, and not lower, than in copper). Hence, also the modulus of elasticity of hard metal powder briquettes (under the same compression pressure) may be lower than in soft metal powder briquettes, even though in the case compact metals the reverse is true.

43. Some Results Proceeding from the Direct Ratio between the Modulus of Elasticity and the Compression Pressure

After having been compressed under the specific pressure p , the ejected briquette expands as a result of the elastic after-

effect, it being the case that the residual stresses (see Paragraph 42) equal σ_p , and the stresses absorbed after the removal of the pressure equal $(1-\theta)p$. In conformance with formula (42/3), the following differential equation will express the expansion of the briquette:

$$\frac{dl}{l} = \frac{\sigma_p}{E} \cdot \frac{d(1-\theta)p}{\theta p} = \frac{\sigma_p}{E} \cdot \frac{d\theta}{\theta} \quad (43/1)$$

where l is the length (height of the briquette, E is the modulus of elasticity of the compact metal.

In integrating equation (43/1), we can assume without any great error (due to the insignificant change in magnitude l) that

$$\int \frac{dl}{l} = \frac{\Delta l}{l}$$

and then obtain

$$\frac{\Delta l}{l} = \frac{\sigma_p}{E} \ln \frac{1}{\theta} \quad (43/2)$$

It follows from (43/2) that the expansion of the briquettes after the removal of pressure $\frac{\Delta l}{l}$ does not depend on the compression pressure and, with the constant magnitude of coefficient θ , it is also constant.

If $\frac{\sigma_p}{E} = 0.01$, and $\theta = 0.01$, the increment in height, induced by the elastic aftereffect, as per formula (43/2), equals 4.6 percent. Such an expansion (of approximately 5 percent) is actually observed in the case of hard metal powders and low-grade powders of medium-hard metals. If $\theta = 0.1$, then, with $\frac{\sigma_p}{E} = 0.01$, the expansion equals 1.3 percent; when $\theta = 0.5$, $\frac{\Delta l}{l} = 0.7$ percent; when $\theta = 0.7$, $\frac{\Delta l}{l} = 0.34$ percent; and when $\theta = 0.8$, $\frac{\Delta l}{l} = 0.22$ percent. In the

case of iron and copper powders of a satisfactory grade, the longitudinal expansion during the ejection from the mold usually fluctuates within the range of 0.3 to 0.5 percent.

Formula (43/1) may be presented as:

$$(1-\theta) p d l = d W = \frac{1-\theta}{\theta} p \frac{\sigma_p}{E} l d (1-\theta) \quad (43/3)$$

where W is the work involved in expansion

In integrating, due to the insignificant change in l , we obtain with approximation:

$$W = p l \frac{\sigma_p}{E} \left(\theta - 1 + \ln \frac{1}{\theta} \right) \quad (43/4)$$

Accepting $\frac{\sigma_p}{E} = 0.01$, and $p = 4000$ kilograms per square centimeter, we obtain that 1 cubic centimeter of the briquette in a longitudinal direction, with $\theta = 0.8$, will be 0.9 kilogram-centimeter; with $\theta = 0.5$, $W = 7.7$ kilogram-meter. This amount of work is insignificant as compared with the work of compression (see Paragraph 52).

44. Ratio between the Toughness of Briquettes and the Compression Pressure and Porosity

Figure 69 below shows the characteristic curves for the ratios between the yield point in compression, the ultimate compressive strength, the expansion along the diameter after ejection from the mold, the relative density of the briquettes, and the compression pressure (approximately "net" pressure).

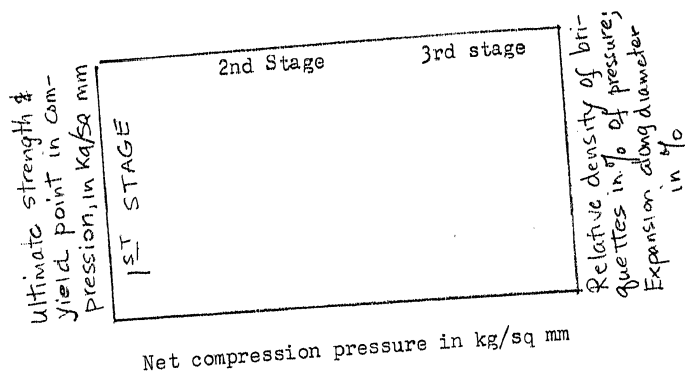


Figure 69. Ratio between the properties of the briquettes and pressure: 1. relative density, in percent; 2. ultimate compressive strength, in kilograms per square millimeter; 3. yield point in compression, in kilograms per square millimeter; 4. yield point in compression, in percent of net compression pressure; 5. expansion along diameter after ejection from press mold -- Electrolytic copper, pouring weight 1.69 grams per cubic centimeter.

The curves showing the ratio between the yield point and ultimate strength in compression and the compression pressure can be divided into 3 rather characteristic sections.

In the first section (low compression pressures), the points of yield and ultimate strength increase more rapidly than with the first power of compression pressure, it being the case that the rate of the growth of strength becomes greater with greater compression pressure. Hence, the curve in this section will have its convexity downward. Such a path of the curve is accompanied by the following peculiarities:

- (1). At this stage, the relative density of the briquette increases very rapidly with pressure, while porosity decreases

just as rapidly.

(2). The expansion of the briquettes after ejection from the press molds is frequently greater than under the medium pressures in the second stage.

(3). Disintegration under compression at the beginning of the first stage usually takes the form of a complete collapse of the briquette into a shapeless powder heap. With higher pressure, the cohesion in the briquette is increased, and, with disintegration, alongside of powder, there are coherent small lumps. At the end of the first stage, disintegration is accompanied by the formation of transverse or longitudinal interparticle fissures (Figure 70 I, II), depending on whether the compression is parallel or normal to the pressure. At times, at the end of the first stage, there occurs the disintegration of cylinders and cubelets of the same type as in the second stage (Figure 70, III, IV).

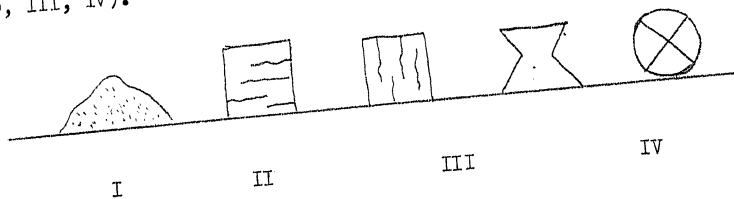


Figure 70. Types of briquette disintegration

In the second section (medium compression pressures), the points of yield and ultimate strength increase linearly with the first power of compression pressure, and this section of the curve is rectilinear. This part of the curve path is accompanied

by the following :

(1). Relative density and porosity of briquettes change with pressure at a much slower rate than during the first stage.

(2). Expansion after ejection from the mold is usually at its minimum during this stage.

(3). During the second stage, rapidly after the yield point has been exceeded, the appearance of "creep" lines at a 30 degree angle to the direction of compression is frequently observed (see Paragraph 41). If compression is continued, the specimens will disintegrate along these lines of creep. During the compression of cylinders (in an axial direction) and cubelets, there is the characteristic formation of two cones (pyramids) at an angle of 30 degrees to the direction of compression (see Figure 70, III). During the radial compression of bushings and cylinders, they disintegrate into four coherent quadrants (see Figure 70, IV). It must be remembered that with further prolonged effect of load, briquettes of even very high density may disintegrate into powder.

In the third section (high compression pressures), the rate of the growth of strength with pressure is constantly diminished, and this section of the curve has its convexity upward. At this stage, strength increases less than with the first power of pressure. The following features are characteristic for the third stage of compression:

(1). Very insignificant growth of density in the briquette

with increase in pressure.

(2). An increase in the expansion of the briquettes after ejection from the press mold with compression pressure.

(3). The briquettes sometimes show fissures after ejection from the press molds even before compressive tests are begun. When pressing in solid press molds, transverse lamellar fissures are observed; when pressing in assembled press molds, the fissures are diagonal.

The relative length of the above first, second, and third sections of the curve runs in relation to the physical characteristics of the powders. The second or the third section of the curve is usually the longest, while the first section is the shortest. The transition from one stage of compression to the next one is practically always gradual, without jumps.

The ultimate compressive strength and the yield point in compression of cubelets is always greater in the direction of compression than in a transverse direction. Under low pressures and densities of briquettes, the difference between longitudinal and transverse strengths is great. Under high pressures, the above difference is diminished. Table 37 indicates the extent of the diminution, with pressure and density, of the ratio between the ultimate compressive strengths in a longitudinal and transverse direction (designated by the author as the anisotropic factor).

TABLE 37

Compressive Strength of Electrolytic Copper Powder, Pouring Weight
2.47 Grams per Cubic Centimeter, in Relation to Compression
Pressure and Density

Compression pressure (gross) in kg/sq mm	Relative density of briquette in %	Ultimate compressive strength, in kg/sq mm in a longitu- dinal direction	in a trans- verse di- rection	Ratio of longi- tudinal strength to transverse strength (anisotropic factor K)
11	56	1.3	0.3	4.3
25	67	5.3	2.5	2.1
100	80	22	20.5	1.1

The values for the ultimate yield point and particularly for compressive strength depend greatly on the shape of the specimens. They increase with the greater ratio of diameter to length.

The constriction of briquettes during disintegration is insignificant and depends little on compression pressure (Footnote. This is easily understood, when taking into consideration that the modulus of total deformation (elastic and residual) is in direct ratio to pressure).

Ultimate tensile strength is usually many times below ultimate compressive strength, but still has a definite mensurable value and at times attains the value of 3 percent of the compression pressure. As per data by Bal'ke, the tensile strength of electrolytic iron powder briquette, formed under a pressure of

205 kilograms per square millimeter, was 6.37 kilograms per square millimeter, i.e., 3.1 percent of the compression pressure, in the case of lead powders, as per Wretblad and Wulff, is shown in Figure 71 below (Footnote. In accordance with the author's terminology, shows the third stage of the tensile strength - pressure curve).

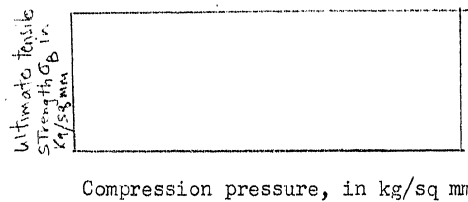


Figure 71. Ratio between the tensile strength of lead briquettes and the compression pressure (as per Wretblad and Wulff)

Elongation and shrinkage in tensile break equals zero. Judging by indirect data (shearing test and observation of the formation of lines of "creep" in compression), tensile strength (in contradistinction to compressive strength) is usually lower in the direction of compression than in a transverse direction.

The ratio between strength and compression pressure can be explained as follows. Powder briquettes are bodies with non-permanent contacts between the particles, it being the case that the value of the residual contact surface is approximately in direct ratio to the compression pressure. The strength of the briquettes is purely mechanical or an engagement strength, stipulated by a mutual interlacing and engagement of the powder particles. Using the terminology by Gubkin⁽²⁶⁾, such strength can be designated as wedging strength. Some part (although a considerably lesser one) may be played by the electrostatic

strength, or the strength of cohesion, stipulated by the effect of the electric forces of cohesion between the atoms of the contact sections. Both strengths are in a direct ratio to the value of the contact surface of a single layer of particles, and, therefore, the total strength of the briquettes has to be in direct ratio to the compression pressure.

Factors exist, however, which cause the departure of this ratio from proportionality.

One group of factors accelerates the rate of the growth of strength with pressure. With pressure, it is not only the contact surface of the particles that increases, but also the density of the briquettes. The strength of the frame made up of the interlaced particles becomes increased not only through the increase in the surface of mutual contact between the particles, in direct ratio to the first power of pressure, but also with the growth in the depth of the interlacing and engagement between the particles, which becomes greater with the density of the briquette. This factor promotes the growth of strength at a more rapid rate than with the first power of compression pressure. With the increase in pressure and density, the coefficient of lateral pressure ξ' is also increased (see Paragraph 31, Table 27). Therefore, the lateral pressure $\xi'p$, which molds the briquette in a transverse direction, increases not in direct ratio to the first power of compression pressure p , but in direct ratio to the product of compression pressure by relative density η , i.e., at a rate greater than with the first power of pressure. With the increase in the form-promoting lateral pressure, the wedging effect becomes increased (simi-

larly to the wedging of an axe in a log). Thus, this factor also promotes the growth of strength (particularly, as can be seen from Table 37, in a direction normal to compression) at a more rapid rate than with the first power of pressure. For purposes of comparison, the graphic data by Karman (114) is shown in Figure 72. Karman conducted compressive strength tests on marble cubelets with the use of additional lateral pressure. He showed that, with the increase in lateral pressure, the compressive strength increased considerably.

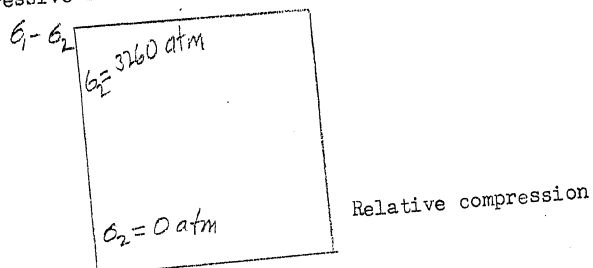


Figure 72. Ratio between compressive strength of marble cylinders and lateral pressure (as per Karman):

- σ_1 - axial compressing stress;
- σ_2 - lateral hydraulic pressure.

This group of factors is linked to the increase in the density of the briquette, and is therefore manifested predominantly during the stage of low compression pressures (see Figure 69, the first stage of the curves indicating the ultimate strength and yield point).

Other factors, inversely, reduce the rate of the growth of strength with pressure. Under high compression pressures (see Figure 69, third stage), density increases rather insignificantly, therefore, the factors which accelerate the rate of

the growth of strength with pressure, play no perceptible part. On the contrary, toughening is manifested to a considerable degree, as a result of which the contact surface increases at a rate lower than with the first power of pressure. Toughening also promotes an increase in the elastic aftereffect (see Paragraph 37). During the third stage, a lesser growth of strength than with the first power of pressure is observed.

Under the medium compression pressures, at the second stage, both the above groups of factors mutually compensate themselves, and there is a linear ratio between strength and pressure.

In compression, external forces counteract the residual stresses and decrease porosity, and in tension, on the contrary, they assist the residual stresses in the disrupting of the briquette and increase porosity. Therefore, strength in compression is always greater than strength in tension. The residual stresses are always greater in the direction of compression, hence, in compression, the strength in the direction of compression is greater (residual stresses counteract the external forces), and in tension, on the contrary, lesser (residual stresses assist in the disrupting).

If we assume that the yield point in compression approximately equals the sum of the residual stresses, then the fraction of the residual stresses in high-grade industrial copper and iron powders can be assumed to be approximately 80 percent of compression pressure. In low-grade powders, this fraction is close to zero in value. Not long ago, Zelig and Woolf⁽¹³⁸⁾

established by X-ray testing that the residual tensile stresses in iron briquettes (gross pressure 75 kilograms per square millimeter) attained the value of 70 percent of the σ_c for soft steel.

45. The Ratio between the Strength of the Briquette and the Properties and State of the Metal in the Powder

Table 38 below depicts the compressive strength of three series of specimens compressed under the same pressure from powders of different metals. To eliminate the possible effect of structural factors, comparisons were made in the case of powders obtained by similar methods and having approximately the same structures and the same relative densities of the poured charge. In the first series, were the powders of tin, copper, and iron obtained by pulverization; in the second were powders of tin, copper, and iron obtained electrolytically; in the third were powders of copper, iron, and tungsten obtained by reduction. The Table indicates clearly the increase in strength (particularly, in a direction transverse to compression), the growth of the anisotropic factor, and the decrease in expansion following ejection from the press mold -- with the increase in the plasticity of the initial metal.

TABLE 38

Ratio between the Compressive Strength of Briquettes and the Metal of the Powder

Powder series characteristics	Type of metal	Compression pressure in kg/sq mm	Relative density of briquette in %	Expansion during ejection in a transverse direction in %	Compressive strength				Ratio between longitudinal and transverse strength (anisotropic factor)
					In a longitudinal direction		In a transverse direction		
					kg/sq mm	in % of pressure	kg/sq mm	in % of pressure	
(Obtained by pulverization - relative density of charge 40 - 50%)	Tin	40	100	0.22	> 50	> 125	> 50	> 125	--
	Copper	40	76	0.34	9.60	24	3.2	8	3.0
	Iron	40	71	0.48	4.2	10.5	0.76	1.9	5.5
(Obtained by electrolysis - relative density of charge 15 - 20%)	Tin	40	99	0.18	> 50	> 125	> 50	> 125	--
	Copper	40	71	0.23	25	62.5	24	60	1.05
	Iron	40	69	0.25	16.4	41	12.8	32	1.3
(Obtained by reduction - Relative density of charge 12-15%)	Copper	40	70	0.25	22	55	20.4	51	1.1
	Iron	40	68	0.27	20.6	51.5	20	50	1.03
	Tungsten	40	63	0.48	2.1	5.02	0.36	0.09	5.8

Such a ratio is due to the following:

(1). With the drop in hardness and critical stress σ_k of the metal, the contact surface of a self-contained layer of particles is increased, hence the same pressure stipulates a greater degree of engagement and mechanical strength in powders of plastic metals (Footnote. The greater strength of soft metal powder briquettes confirms the opinion, according to which strength is stipulated predominantly by engagement and not by cohesion. Were strength determined by cohesion, the reduction in the contact surface, in the case of metals, would be compensated by a corresponding increase in the strength of cohesion per unit of contact area).

(2). With the increase in plasticity, the elastic after-effect is reduced.

(3). With the increase in plasticity, the coefficient of lateral pressure ϵ is usually increased.

(4). With the increase in plasticity, the density of the briquettes is increased. It must, however, be underscored that the greater strength of soft metal powder briquettes cannot be explained by the differences in density only. Even with the same density of briquettes, as demonstrated experimentally by the author, the strength of tungsten briquettes was considerably lower than the strength of iron and copper briquettes (although the promoting compression pressure was, on the contrary, considerably greater).

Conformantly with the above, the cold-hardening of the

metal, in lowering its plasticity, reduces the strength and increases both the expansion during ejection from the press mold and the anisotropic factor. The annealing of the cold-hardened metal, in raising its plasticity, on the contrary, increases the strength and reduces both the anisotropic factor and the elastic aftereffect (see Figure 73).

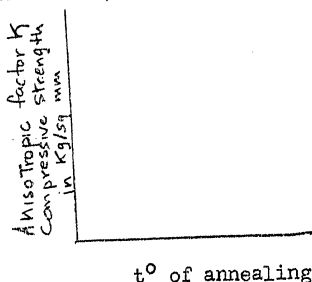


Figure 73. The effect of preliminary annealing of the powder upon the properties of the copper ore concentrate slime briquettes: 1. compressive strength in a longitudinal direction; 2. the same, in a transverse direction; 3. anisotropic factor (ratio between strengths in different directions).

In addition to the reduction in hardness, the favorable effect of annealing can also be explained by the reduction of the oxides. Of some importance during a low-temperature annealing is the reduction in the pouring weight of the powder, and during high-temperature annealing is the increase in the equiaxiality of the particles and the formation of the intraparticle pores.

The experiments conducted by the author with powder mixtures of various metals have shown that the actual strength of the

mixture compressed from various metals is frequently lower (not too perceptibly) than the strength of briquettes computed by the rule of additivity in accordance with the strengths of briquettes from the mixture components. The elastic expansion during ejection from the press mold, on the contrary, is greater than the value computed by the rule of additivity. Sometimes, mixtures will result in briquettes with lamellar fissures, although briquettes made from the initial materials showed no fissuring. Such an example (iron-graphite mixtures) was already cited in Paragraph 10. Some examples of diminished strength as a result of mixing are cited in Table 39.

The causes of this phenomenon are as follows. In places of contact of particles of different hardness, the specific pressure upon the contact area always equals the critical stress of the softer metal, resulting in the deformation of the soft metal particles only. When the contact is between the particles of one metal, all particles are subject to deformation, as a result of which the strength of the briquettes will be greater. A number of examples may be cited that will show the contact subject to unilateral deformation to be weaker than the one subject to two-way deformation. If a nail in being driven into a board would not be subject to deformation, it could be pulled out of the board with much less effort than is actually required. It is easy to split a log with a hard steel axe, the blade of which does not become deformed, while it is not possible to do it with a wooden axe, which itself becomes deformed upon impact. In the compression of a briquette consisting of a mixture of powders of two metals, the harder particles act as non-deform-

able wedges, splitting the contact between the particles and facilitating disintegration.

TABLE 39

The Strength of Mixtures of Powders of
Different Metals

Initial powder	Compression pressure, in kg/sq mm	Crushing strength, in kg/sq mm	Strength com- puted by rule of additivity kg/sq mm	Expansion along the diameter, in %	
				by rule	of addi-
				Actual	tivity
Electrolytic copper	40	25	--	0.23	--
Electrolytic iron	40	16.4	--	0.25	--
Copper and iron mixed 1:1	40	16.2	20.7	0.26	0.24
Electrolytic copper	40	25	--	0.23	--
Reduced Tungsten	40	2.1	--	0.48	--
Copper and Tungsten mixed	40	8.3	13.55	0.40	0.355

It must be remembered that, in contradistinction to single metal powders, an annealed metal mixture powder (such as copper and zinc, copper and tin, and the like) almost invariably worsens compressibility and reduces the strength of briquettes. This is due to the fact that the solid solutions and intermetallic compounds that are formed are considerably harder than the mixture of pure metals.

46. The Effect of Admixtures and Additions Upon the Strength of the Briquettes

In the presence of a considerable content of oxides, the strength of the briquette is considerably reduced. This is due to the following causes:

(1). With a considerable content of oxides (5 to 10 percent volumetrically and higher), the contact area is determined by the critical stress σ_R of the hard surface layer of oxides, as a result of which (and in a number of cases also due to poorer compressibility) the contact surface is reduced.

(2). An increase in the elastic aftereffect (a greater hardness and a smaller strength of the surface layer).

(3). A reduction in the mechanical strength of the surface layer (regardless of its greater hardness).

An insignificant amount of oxides affects the strength of the briquette to a much smaller extent. Additions introduced into the powders in order to reduce the friction against the walls of the press mold (liquid and solid lubricants, glycerin, paraffin,

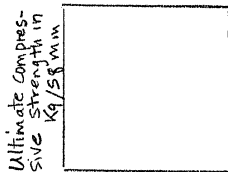
and stearic acid) usually attenuate the strength of the briquette to a small degree only (10 percent or less). This also confirms the opinion that the strength of the briquettes is stipulated by the engagement of the particles and not by cohesion, since the above enumerated additions reduce cohesion substantially (by several times).

47. The Effect of the Volumetric Characteristic and the Structure of the Particles upon the Strength of the Briquettes

The strength of single metal powder briquettes greatly depends on the structure and the volumetric characteristic of the powders.

As already indicated (Paragraphs 13 and 23), light powders of low pouring weight always have greater strength than heavy powders.

Therefore, with the same relative density of briquettes, compression pressure and, consequently, the contact surface of a self-contained layer of particles, is greater in the case of light-weight powders. Hence, given the same porosity, the strength of light-weight powder briquettes is considerably greater than that of the heavy powder briquettes (see Figure 74).



Pouring weight, in grams per cubic centimeter

Figure 74. The effect of the pouring weight upon the strength of copper briquettes: 1. with relative density the same (69 percent); 2. with compression pressure the same (40 kilograms per square milli-

meter).

If strength is expressed as a fraction of compression pressure (Figure 74), this fraction will also increase with the drop in the pouring weight of the powder. Thus, the greater strength of light-powder briquettes cannot be due exclusively to higher compression pressure. Seemingly, a better interlacing and engagement of the particles of the light-weight powders, which have a rougher surface, plays its part. The non-reversible engagement of the powder particles is sometimes facilitated by their more pronounced "surface" (see Paragraph 13) and intra-particle porosity. A considerable part is also played by the elastic aftereffect, the detrimental effect of which is less pronounced in the case of light-weight powders with tough mutual engagement of the particles. The differences in strength as between light-weight and heavy-weight powder briquettes are particularly great at high porosity. At low porosity, these differences are reduced (in these cases, the net pressures are almost the same and approximate the critical pressure σ_k), yet they do not disappear completely.

The structure of the particles exerts a considerable effect upon the strength of the briquette. Minimum strength and maximum elastic aftereffect are manifested by briquettes with smooth equiaxial and smooth flat particles. Maximum strength and minimum expansion upon ejection from the press mold is observed in briquettes with rough dendritic and acicular particles, and also in the presence of internal pores in the particles (see Table 38).

Frequently, the powders with a structure of particles particularly unfavorable to the strength of the briquettes are at the same time the heavy-weight powders. This, however, cannot be construed as a rule. For instance, copper powders, pulverized in a stamp mill (copper ore concentrate slime), have a low pouring weight and at the same time a low strength (particularly, in a direction transverse to compression). This is due to the unfavorable orientation of the particles, with their wide side normal to the pressure, which promotes the formation of transverse lamellar fissures.

This defect can be rectified by associating the particles into conglomerates.

The diagram in Figure 75 shows how the association of the particles into conglomerates cancels out the unfavorable orientation of the particles (with their wide cross section perpendicular to the compression pressure).



Figure 75. Diagram explaining the effect of the association of particles into conglomerates: on the left, compression of non-associated particles; on the right, compression of associated particles.

Such an association into conglomerates may be accomplished for example, by the addition of gluing substances. Figure 76 (Microphoto) shows that, upon the addition to the poured charge of a gluing substance (rubber in gasoline), the unfavorable ori-

entation of the particles in the copper ore concentrate slime (see Figure 38) disappeared, and in its place appears a haphazard eddying of particles in glued lumps. The association of particles into lumps of about 0.1 to 5 millimeters in size, under conditions of high-temperature annealing, has a still more favorable effect.

Microphoto

Figure 76. Pressing a charge of copper ore concentrate slime powder containing a gluing substance -- longitudinal section, in the direction of compression -- x 500 times

In the past, the majority of the scientists assumed that fine particles should produce greater strength in briquettes, since the total contact surface is in an inverse ratio to the diameter of the particles. Such an opinion was held by Sauerwald, Rakovskiy, and many others.

However, although the total contact surface of all particles increases in an inverse ratio to their diameter, the contact surface of a self-contained layer of particles (see Paragraph 16), which determines the strength of the briquettes, depends not on the degree of dispersion of the powder, but only on the compression pressure. Experiments by the author proved that the size of the particles in most cases has only an indirect effect upon the strength of the briquette. If, with a reduction in the degree of dispersion, the pouring weight became increased, strength was diminished. But if, with a reduction in the degree of dispersion, the pouring weight remained the same, or was also reduced, the strength, on the contrary, became greater. For instance, briquettes from fine

particles of pulverized cast iron had a lower strength than briquettes from cast iron chips.

Figure 77 is a curve graph representing the strength of briquettes from reduced iron grit in relation to the size of the pieces. The pouring weight of all the fractions of the grit was the same (1.4 grams per cubic centimeter), and the density of the briquettes from the fractions of various size, compressed under the same pressure (40 kilograms per square millimeter), differed only within the limits of measuring precision (by ± 3 percent). It can be seen clearly that, with the exception of the finest fraction (less than 0.1 millimeter), strength is increased with the size of the grit.

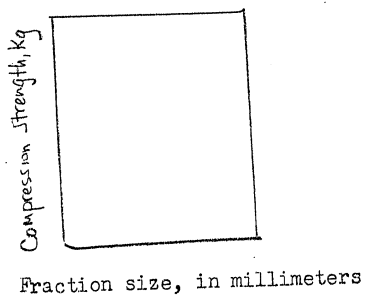


Figure 77. Ratio between the compressive strength of briquettes and the particle size of iron grit

The growth of strength with the magnitude of the particles was already explained by the author long ago⁽²⁾. From a purely geometrical viewpoint, large-size particles are conducive to strong briquettes (see Figure 78). The disintegration of briquettes is always accompanied by the formation of interparticle fissures. In the presence of fine particles (see Figure 78A),

the formation of interparticle fissures is facilitated, in the presence of coarse particles (see Figure 78B) -- it is greatly inhibited.

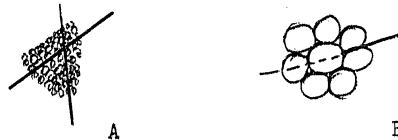


Figure 78. The effect of geometrical factors upon the disintegration of briquettes: A. fine powders, fissures form easily; B. coarse powders, geometrical factors inhibit the formation of fissures

The higher strength of specimens from the very finest fractions of a powder is due to the better mutual abutment between the very finest particles. A cable coiled from fine wire can easily be wound around a pillar, but the same cannot be accomplished with a thick rod. Any object can easily be wrapped in paper, but not in cardboard, and the like.

48. The Effect of the Compression Rate

Publications on the subject contain contradictory statements relating to the effect of the rate of compression upon the strength of the briquette. Hardy⁽⁹⁸⁾ and Rostarchuk are of the opinion that both the strength and the density of briquettes increase with the rate of compression, ascribing the cause to the smaller volume of air entrapped during a higher rate of compression. Balke⁽⁷⁸⁾ and Greenwood, on the contrary, assume that with a higher rate of compression, both the strength and the density of the briquettes are decreased. They ascribe the cause to the same air, with the only difference that, in their opinion, it is the

slow rate of compression that entraps a smaller volume of air.

In the opinion of the author, the effect of the rate of compression is made up of various factors.

On the one hand, a reduction in the rate of compression may result in a tighter disposition of particles. A certain amount of time is required for the shifting and deformation of the particles. Hence, in some cases, with the diminution in the rate of compression, density and strength will increase somewhat. This is particularly noticeable when the temperature of compression approximates the temperature of recrystallization, under which conditions the phenomena of creep may be manifested (the pressing of lead and tin at room temperature, also hot-pressing).

On the other hand, slow compression disintegrates to a greater degree the oxidized surface contact layer of the particles. This should accelerate the elastic aftereffect and somewhat reduce the strength and density of the briquettes, as demonstrated by the following test conducted by the author. Copper powders were compressed at different rates to a constant volume of 1 cubic centimeter. Upon ejection from the press molds, the rapidly compressed powders manifested a lower expansion as a result of the elastic aftereffect (see Table 40 below).

TABLE 40

The Effect of the Rate of Compression upon
Expansion after Ejection and upon the
Strength of Electrolytic Copper Powder Having
a Pouring Weight of 1.80 Grams /Cubic Centimeter

<u>Speed of compression</u>	<u>Volumetric</u> <u>expansion of</u> <u>briquette after</u> <u>ejection, in %</u>	<u>Relative</u> <u>density of</u> <u>briquette</u> <u>in %</u>	<u>Compressive</u> <u>strength,</u> <u>in kg/sq mm</u>
(In hydraulic press			
(1 minute	0.8	69.5	9.8
(Impact compression			
(in friction press	0.5	69.6	11.3

The correctness of the author's opinion is also confirmed by the Kantorovich data pertaining to the measuring of the electrical conductivity of the briquettes (Footnote. The explanation that follows is the author's; Kantorovich was not explaining the results he obtained). Kantorovich observed a pronounced increase in electrical conductivity with a time lag under pressure (see Table 34). In the author's opinion, this result is due to a reduction in the strength and to the disintegration of the surface layer of particles during the time lag. By the same token, the compression time lag and the reduction in the rate of compression resulted in a higher resistance during the discontinuation of the pressure and recompressions (considerably reducing thereby the

strength of the surface contact layer of particles).

According to Jones, an intensive heating of the contact layer of particles occurs with rapid compression. This heating promotes the reciprocal welding of the particles and the growing strength of the briquettes. Jones even allows the possibility of the liquifaction of the contact layer. However, a simple computation proves the Jones assumptions to be greatly exaggerated.

Let a briquette with a cross section area and a "reduced" volume, equal to unity, have, under the specific pressure p , a relative volume B . The increment in pressure from p to $p + dp$ will reduce the relative volume by dB . Then, the increment of the work involved $dw = p dB$. The work of compression induces an equivalent liberation of heat, which will raise the temperature of the briquette. Assuming the speed of compression to be infinitesimal, this heat will be consumed for the heating of the entire volume of the briquette B , also of the press mold and of the surrounding medium. Assuming the speed of compression to be infinitely great, the liberated heat will only raise the temperature of the deformed volume dB that is contiguous to the contact sections. In the latter case, the specific work of compression per unit of deformed volume dB , is $\frac{dw}{dB} = p$, and the temperature increment $\Delta t = \frac{p}{J \gamma_{\text{spec}} c}$, where γ_{spec} is the specific gravity in grams per cubic centimeter, c is the specific thermal capacity, J is the mechanical equivalent of heat. Specifically, if we take the case of the compression of a copper powder, for which $\gamma_{\text{spec}} = 8.93$ and $c = 0.0911$, then, under a specific pressure of 5000 kilograms

per square centimeter and an infinitely great speed of compression, $\Delta t = 144^\circ$ Centigrade. Under an infinitesimal speed of compression, the entire amount of heat is eliminated, and $\Delta t = 0$. Practically, however, the difference in the temperature of the contact sections, as between rapid and slow compression, hardly exceeds 30 - 50° Centigrade.

Nevertheless, even this temperature may play a certain part in increasing the strength of the briquette at the expense of heating up the water-containing "argillaceous" layer of oxides.

In the pressing of mixtures consisting of powders of various metals, slow compression may worsen the properties of the briquettes by promoting the "liquation" of particles.

Table 41 below is a compilation of data by Shpagin⁽⁷³⁾ showing an increase in the density and the strength of the briquette with the acceleration of compression.

Generally speaking, the speed of compression has no particularly perceptible effect upon strength. As will be shown further down in the text, rapid ejection from the press mold favorably affects the quality of briquettes.

Thus, the acceleration of compression, in most cases, has no negative effect upon the quality of the products.

TABLE 41

The Effect of Compression Speed on the Quality of Briquettes Consisting of 50 Percent Copper and 50 Percent Graphite, with Pressure at 20 Kilograms per Square Millimeter

<u>Duration of compression</u>	<u>Density in gr/ cu cm</u>	<u>Shor hardness</u>	<u>Ultimate compressive strength in kg/sq mm</u>
20 minutes	3.07	13	0.0
8 minutes	3.07	13	0.5
4 minutes	3.08	13.3	0.6
50 seconds	3.09	17	0.6
15 seconds	3.10	17	0.8
10 seconds	3.13	17	0.5

Causes for Flaws and Rejects

The most serious and widespread type of flaw in the compressed semifinished products is the so-called exfoliation -- the appearance of interparticle fissures in the specimen upon being extracted from the press mold.

In the pressing of products in non-detachable press molds, the appearance of transverse lamellar fissures is observed sometimes after the ejection of the briquette from the press mold. The main cause of this exfoliation, in the opinion of the author, is the effect of internal stresses (elastic aftereffect) accumulated during the process of compression. Since these stresses attain their maximum value in the direction of compression, transverse fissures are formed.

A few words about the factors which promote exfoliation.

(1). All factors attenuating the strength of the briquette, such as the presence of oxides, the presence in the powder charge of non-metallic components (graphite), unfavorable structure (smooth particles, flat particles), a high degree of hardness of the initial powder particles, and the like, are conducive to exfoliation.

(2). Excessive fineness of powders may facilitate fissuring (see Paragraph 47, Figure 82).

(3). Excessive pressure. Internal stresses, which are conducive to fissuring, always grow in direct ratio to compression pressure, while strength, under high pressures, increases at a slower rate than pressure [lags behind] (see Paragraph 44).

(4). The improper design and defects in the press mold. When the design of the press mold does not provide for the gradual expansion of the briquette during ejection, the appearance of shearing stresses will be conducive to the formation of transverse fissures during ejection. Figure 79 below shows the effect of such abrupt expansion upon the formation of fissures in an exaggerated manner. It is imperative to provide for the widening of the egress end of the press mold by a taper of 0.5 to 1 degree to the axis. The improper condition of the press mold walls is also conducive to fissuring.

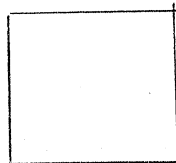


Figure 79. The effect of the press mold design upon the formation

of fissures in the briquette (diagram).

(5). Slow ejection. Figure 79 shows clearly that when the speed of ejection is infinitely great, no fissures will appear, while an infinitesimal speed of ejection, on the contrary, will promote their formation.

(6). An excessively low rate of compression. (see Paragraph 48)

When pressing in detachable press molds, diagonal fissures are sometimes formed. The usual cause of their appearance is the shift of a side wall (due to improper wall bracing, or defect in design, or excessive pressure) and the disintegration of the briquette under pressure.

Briquette Hardness

Figure 80 below is a curve graph representing the ratio of the Brinell hardness of the briquette to the compression pressure. As indicated by the curves, in the presence of low pressures, hardness grows almost in direct ratio to the first power of pressure (sometimes even faster than with the first power of pressure). Under high pressures, hardness grows considerably slower than with the first power of pressure. Thus, there is a ratio of the same type that prevails in the case of the strength of the briquette (see Paragraph 44). However, the growth of hardness departs from the direct ratio to a greater degree and under lower pressures than does strength. The reasons for this phenomenon are as follows.

Brinell hardness, as indicated by Kunin⁽³⁹⁾, runs in an

approximate direct ratio to the work consumed for the non-reversible deformation of the metal in a unit of imprint volume. It may be assumed that the Brinell hardness of the briquettes is approximately in direct ratio to the specific work of compression. This work, in conformity with formula (28/9), is theoretically proportional to the compression pressure. However, due to toughening, the work grows not as rapidly as pressure (if force p increases with toughening, the path, along which the force Δh performs some work, decreases). In the consolidation of the briquette to a relative density $\rho = 100$ per cent, p may grow infinitely, while the increment of the work of plastic deformation equals zero, since the non-reversible change in the height of the briquette $\Delta h = 0$.

The direct ratio of strength to compression pressure is also somewhat disturbed due to the effect of cold-hardening (see Paragraph 45). This departure is, however, compensated for to a considerable extent by the oppositely-directed effect of the increase in density. On the contrary, there exists a series of factors intensifying the reducing effect of toughening upon the growth of hardness with pressure. Let us take note of the most important of them.

(1). In determining the Brinell hardness of a non-consolidated briquette, the work of penetration by the test ball is consumed both for the displacement of the deformed volume of the metal as well as for the additional consolidation and toughening of the powder particles. In the case of a consolidated bri-

quette, the work of penetration by the test ball is consumed only for the displacement of the deformed volume. Hence, an increase in density, while increasing the growth of strength with pressure, may reduce the growth of hardness.

(2). All researchers were determining hardness (see Figure 80) at the strongest and densest upper surface of the specimen, which was nearest to the plunger. While the values of strength are stipulated (in relation to the direction of compression) by the mean strength in the entire volume or by the strength of the weakest and the non-consolidated cross section. Hence, the effect of toughening will manifest itself to a greater extent upon hardness than upon strength.

The hardness of briquettes is subject to the following regularities.

(1). Hardness grows with compression pressure, density, and the strength of briquettes. Maximum hardness at maximum density corresponds approximately to the maximum critical stress $\sigma_{\max}$ of the material.

(2). The hardness of briquettes is to a considerable degree a contact interparticle property (particularly in the presence of low pressures and densities). When briquettes from different metal powders are compressed under the same pressure, the softer metal powder will, in most cases, result in the harder briquette. Even when comparing specimens compressed to the same density, the soft metal powder will frequently result in a briquette of greater hardness (regardless of the lower compression pressure).

(3). Hardness is anisotropic; it is less in a transverse direction than in a longitudinal direction. This is particularly noticeable when hardness is determined by the Shor method (see Figure 57). Such anisotropy is due to the fact that, in a longitudinal direction, the shaping pressure is greater, while the cross section of particles and porosity, on the contrary, are less.

(4). Hardness differs in various spots of the briquette, by height, in conformity with non-uniform density (see Figure 57).

(5). The hardness of briquettes under the same compression pressures usually grows with the reduction in the pouring weight of the powder (particularly during the first stages of compression). This is due to the fact that the specific work of compression, which is equal to $\frac{P}{m-1}$, is greater in the case of light-weight powders (the magnitude of the compression index m , which is a part of the denominator, decreases with the diminution in the pouring weight of the powder).

51. Is There a Qualitative Difference between Compressed and Non-Compressed Powders?

The numerous published opinions of specialists relating to free-flowing bodies and the nature of their strength and cohesion, may cause a serious disorientation in this field. Let us quote, as typical, the opinions by Professor Prokof'yev⁽⁵²⁾:

"There is no cohesion between particles of free-flowing bodies, as a result of which, in contradistinction from solid bodies they cannot sustain tensile stresses, but there is friction between the particles of a free-flowing body. As a result of this friction

the particles may maintain equilibrium within a certain range, until such time as the friction between individual articles is disrupted! (Prokof'yev).

Prokof'yev also maintains that only compressive normal stresses (σ) can exist in free-flowing bodies, while tensile stresses are absent, and the tangent (shearing) [stresses] $\tau = \mu \sigma$, where μ is the coefficient of friction. The shape of free-flowing bodies, according to Prokof'yev, is always limited by the angles of natural repose, φ .

Opinions of this type, characteristic of all the specialists on free-flowing materials from the days of Coulomb to the present, are badly in need of a basic revision.

If the point of view of these specialists is accepted, it becomes necessary to acknowledge that between loose powders which have the form of a heap at the angle of natural repose, and do not sustain any tensile stresses, and compressed powders, which may have any shape and do sustain tensile stresses, there is a tremendous qualitative and basic difference.

Actually, the assertion that free-flowing bodies do not sustain any tensile stresses, that being their characteristic, is utterly wrong. The most characteristic feature of free-flowing materials is the inconstancy in the magnitude of the contact surface between the particles, which is a function of the external stresses. Hence, their mechanical properties, including tensile strength, are a function of the shaping pressure, which, in this case, is the weight of its particles. The absence of cohesion,

in this case, as well as in the case of briquettes, cannot hinder the existence of a definite tensile strength stipulated by the reciprocal engagement of the particles. This strength is expressed by the formula:

$$\sigma_b = \Theta \sigma_\phi \quad (51/1)$$

where σ_b is the tensile strength, σ_ϕ is the shaping pressure (in this case, the stress, to which a unit of the cross section area, breaking under the weight of the particles, was subject), Θ is a more or less constant factor, always less than unity (in the case of briquettes, the value of Θ is usually 1 percent and less).

Since Θ is always considerably less than unity, it is impossible, under usual conditions, to measure the tensile strength of free-flowing materials, as shaped under the effect of their own weight. But free-flowing materials shaped under pressure greater than their own weight, can be made to assume variegated forms, and they have a fully mensurable tensile strength σ_b . But always $\sigma_b < \sigma_\phi$.

If this viewpoint, advanced by the author, is accepted, i.e., a free-flowing material is a body with an inconstant contact between its particles, the body being shaped under the effect of its own weight, it will become clear that between briquettes, shaped under high pressure, and loose powders, there are only quantitative, but not qualitative differences. These quantitative differences have a value of approximately the same order as the difference between compression pressure and the weight of the free-flowing body, i.e., in compression the properties (strength,

hardness, electrical conductivity, the contact surface area) increase from 10^3 to 10^6 times.

A series of facts confirm the correctness of this, as follows.

(1). The contact surface in both compressed and loose powders is stressed, it being the case that the magnitude of critical stress σ_k , if the effect of toughening is disregarded, is fully the same in both cases.

(2). The powder particles begin to sustain deformation already under the effect of their own weight. By slightly shaking 100 grams of a fine copper powder over a period of one hour, its pouring weight was increased from 0.40 to 0.64 grams per cubic centimeter. This increase in pouring weight was a result of the non-reversible brittle and plastic deformation of the surface layer of the particles. In this respect, the compression pressure does not introduce anything qualitatively new, but only accelerates quantitatively already existing phenomena.

(3). The orientation of the particles already exists in the loose powders, and the compression pressure only somewhat accelerates its effect.

(4). The study of compression curves (pressure-deformation curves) shows the absence in them of any abrupt change which would indicate the transition from a non-cohesive powder to a cohesive briquette. From the lowest to the highest pressures there is a smooth and gradual increase in pressure with deformation.

The curves for the mechanical properties of the briquettes

show a gradual growth of strength, approximately in direct ratio to the pressure and without abrupt changes. The extrapolation of these curves shows the coincidence of zero strength with zero pressure. Thus, to all appearances, strength, including tensile strength, also exists in loose powders. However, due to the low value of the shaping pressure, it is thousands and millions of times below the strength of briquettes.

52. The Cold-Pressing Process from the Angle of Energetics

It would seem at first that a non-consolidated powder should be in a state of lesser equilibrium than a briquette reduced by compression to full compactness. In the loose powder, the forces of cohesion may perform the work of drawing the particles together, while in a compact body, this work has already been performed. Actually, however, a compressed powder is in less stable equilibrium and has a greater reserve of free energy, as compared to a loose powder. This is due to the fact that, in compression, there takes place work against the forces of cohesion, and not work by the forces of cohesion.

Some researchers assume erroneously that compression is linked with work performed by the forces of cohesion, and not against those forces. In the opinion of Rakovskiy⁽⁵⁴⁾, it takes less pressure to compress fine powders than coarse ones, since the cohesion forces promote to a greater extent the drawing together of the fine particles with a better developed specific surface. Actually, the phenomena usually observed show that the reverse is the case. Already under the effect of their own weight, the fine powders practically always occupy a more friable

7

volume than the coarse powders, and, with further consolidation, higher compression pressures are required for fine powders. Jones⁽²⁷⁾ maintains that the absence of spontaneous drawing together between the powder particles at room temperature is, to a certain extent, due to the presence of surface admixtures reducing the effect of the cohesion forces. Again, the reverse of this is actually true. During the reduction of surface oxides, the surface forces of cohesion are increased, yet the volume occupied by the powder becomes greater and not smaller. Inversely, during oxidation, the cohesion forces are decreased, and the volume of the powder is reduced. The practical men do the smart thing by introducing into the powder charge, for the purpose of facilitating compression, additions that reduce cohesion.

Cohesion between the atoms of tungsten is much greater than between the atoms of tin. The very fact that in order to consolidate a tungsten powder it takes a considerably higher pressure and many times the work, as compared to the case of tin powder, is adequately convincing evidence that, in compression, work is performed against the forces of cohesion. In order to bring into contact a relatively low number of surface atoms, it is necessary to deform a volume, which is occupied by a much higher number of atoms, or, which is the same, to disrupt the equilibrium between the forces of cohesion of these more numerous atoms. Hence, in order to attain consolidation, it is necessary to disrupt the equilibrium between the forces of cohesion of both the surface layers of the contact sections, as well as in the deeper volume, with the result that the compressed powder is in

less stable equilibrium and has a greater reserve of free energy than the loose powder. In loose powders (if the presence of admixtures are disregarded), only the surface atoms, i.e., considerably less than 1 percent of all atoms, are in a state of non-equilibrium. In a powder compressed to full compactness, the entire volume has undergone deformation, and is in a stressed state, hence, the non-stable equilibrium extends to the entire 100 percent of the atoms.

The atoms have low mobility at room temperature, and the forces of cohesion between them can then be considered practically as static forces of constant magnitude and direction. In conformity with the literal meaning of the word, the forces of cohesion, during cold-pressing, are forces that superimpose chains and tend to maintain the established equilibrium (even though this intermediate equilibrium may be less stable than the final equilibrium). The stronger these chains, the greater force and the greater the amount of work are required to break them. Specifically such work against the cohesion forces is performed in cold-pressing. Other possibilities for consolidation consist, on the contrary, in the weakening of these forging forces and in creating for them such conditions, under which they themselves would perform the work of consolidation. Such phenomena occur during the process of baking, when the interaction forces between the atoms are attenuated and acquire dynamic characteristics.

In cold-pressing, the "reduced" work W_k , i.e., the work performed to compress 1 cubic centimeter of compact material, is expressed, in accordance with formulas (28/8) and (28/9):

$$W_k = \frac{p}{(m-1)\rho},$$

where p is the specific compression pressure, m is the compression index, ρ is the relative density of the briquette. The computation of this work, in the case of copper, under practically occurring pressures (1000 to 6000 kilograms per square centimeter), relative densities (50 to 90 percent), and compression indexes m (2.5 to 7), results in values of W_k from 3.3 to 45 kilogram-meters per cubic centimeter. By recomputing this work in terms of heat, we see that under the practically applied pressures the work of compression corresponds to heating the copper to from 10 to 130 degrees Centigrade, i.e., many times less than the energy imparted to the briquette in baking (usually the baking temperature for copper is 700 to 800° Centigrade).

CHAPTER VIII

INTRODUCTION TO THE THEORY OF BAKINGThe Mobility of the Atoms and Its Change in the Process of Heating

The force of reciprocal attraction and repulsion between two atoms (molecules) at a constant temperature, in conformity with formula (5/1), depends on the distance between them:

$$P = \frac{a}{r^m} - \frac{b}{r^n},$$

where P is the force of interaction; a, b, m, n are constants; r is the distance between the atoms; $\frac{a}{r^m}$ is the force of gravity; $\frac{b}{r^n}$ is the repelling force.

The atoms (molecules) are not immobile, but are in an oscillating motion about the mean position of equilibrium. The range of these oscillations increases with temperature.

Hence, with a rise in temperature the interatomic (molecular) forces progressively lose their static characteristics and become dynamic. During the oscillations of the atoms, the distance r is alternately increased and decreased. Conformantly, as follows from formula (5/1), the interatomic forces are alternately decreased and increased. Generally speaking, the increase in the mobility of the atoms in heating leads to the attenuation of the forces of cohesion, the increase in the volume of the body and the parameter of the lattice, and the growth of the coefficient of thermal expansion, as presented graphically in Figure 81, in accordance with Koch and Dieterle, and Koch and Danecker⁽¹¹⁶⁾. The diminution in cohesion (growth of repulsion) with temperature can be computed by deducting

from the resultant force P in formula (5/1) the term $\frac{c(T)}{r^2}$,
 where $c(T)$ is some function growing with temperature, T ; l is a
 constant; we then derive formula (5/2):

$$P = \frac{a}{r^m} - \frac{b}{r^n} - \frac{c(T)}{r^2}$$

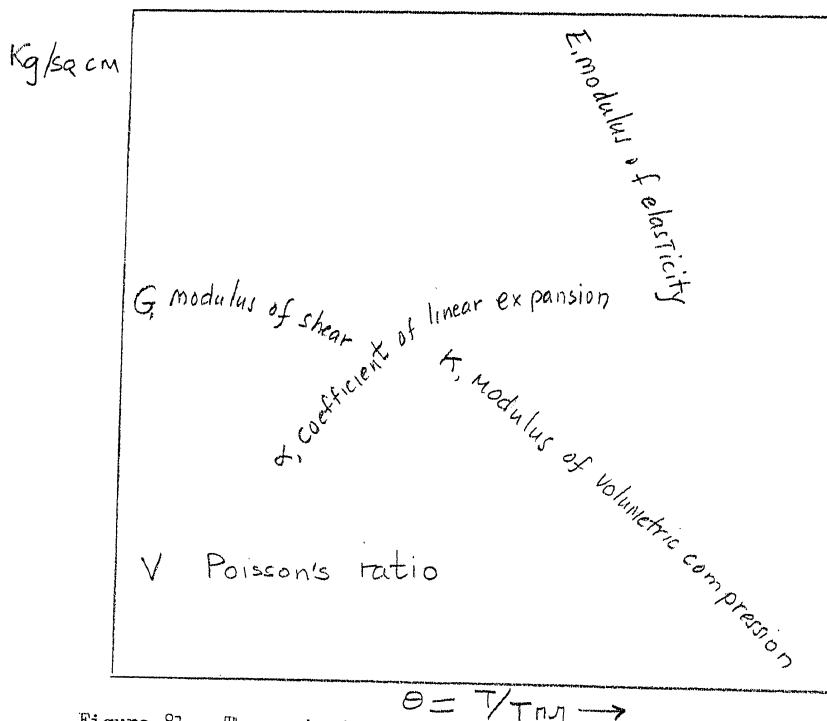


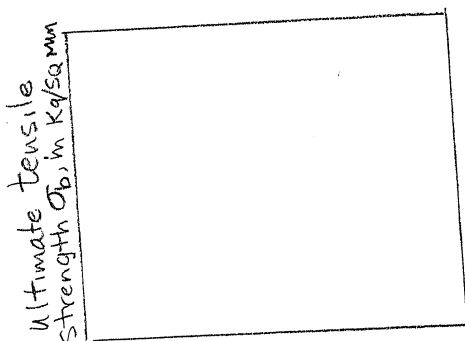
Figure 81. The mechanical properties of aluminum in relation to
 temperature (as per Koch and Dieterle, Koch and Danecker)

The increase in the mobility of the atoms and the attenuation
 of cohesion between them produces an effect, by virtue of which the
 metal being heated, even prior to attaining its melting point, loses
 to some degree the properties of a solid body and acquires the pro-
 perties of a liquid. For instance, its Poisson's ratio ν (see
 Figure 81) continuously grows with temperature and converges toward

the value $\nu = 0.5$, which is characteristic for a liquid. The strength of the metal, in heating, is greatly reduced (by several times ten), as can be seen from the curve graph in Figure 82, as per Ludwik⁽¹²²⁾. The same ratio is true with relation to hardness. According to Ludwik, who tested the hardness of metals by the impressions left in the metal by a test cone, the hardness in heating, changes as per formula

$$H = H_0 \left(1 - 1.23 \frac{T}{T_{\text{пл}}} \right), \quad (53/1)$$

where | H is the hardness at a given temperature;
 H_0 is the hardness at absolute zero;
 T is the absolute temperature of the test;
 $T_{\text{пл}}$ is the absolute melting point. By formula (53/1) hardness becomes equal to zero already at a temperature of about 81 percent within the melting point range.



Temperature, in °C

Figure 82. Ultimate tensile strength of aluminum in relation to temperature (as per Ludwik)

In reality, in contradistinction to liquids, the strength and hardness of which are zero, the above properties in a solid body, even though near its melting point, have a certain, however small, yet a perceptible finite value. Thus, ice floating in water at 0° Centigrade has a perceptible strength and hardness. Surface tension in solid bodies, as presented graphically in Figure 83 in accordance with Tammann and Boehme⁽¹⁴⁷⁾, also decreases with temperature, although at a slower rate than strength.

Footnotes. The fact being that the strength of liquids equals zero, no deduction must be drawn to the effect that cohesion and the forces of cohesion between its atoms are also equal to zero. Surface tension, stipulated by tangential forces of cohesion, has a considerable magnitude in liquids.

It must be noted that Tammann and Boehme were not entirely right in determining the surface tension by the magnitude of the force required to prevent the warping of gold leaflets, without taking into consideration their own strength. When the latter is accounted for, the differences in the changes of surface tension and strength with temperature are considerably reduced, but they still remain.

Hence, with heating, the relative importance of surface tension in the formation of solid bodies is increased, while the relative importance of strength is decreased. In this sense, a solid body, with the progressive increase in temperature, progressively approaches the state of a liquid, in which surface tension is of decisive importance in the formation of drops.

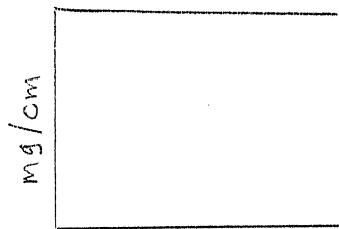


Figure 83. Surface tension in gold in relation to temperature

The elastic properties of the metal, such as the moduli of elasticity, shear, and volumetric compression, also diminish with temperature, but at a considerably slower rate than strength (see Figure 81).

If the properties of the crystal throughout its volume, with temperature, approximate the properties of a liquid, the same will be true to a greater degree about the surface layers of the crystal, where the atoms have maximum mobility. The atoms in the surface, as shown in Table 42 below, are surrounded by a lesser amount of neighboring atoms, attracting them, than they are deep within the crystal.

The less bound the atoms, the more mobility they have. Hence, the atoms inside the crystal and inside the contact sections of the surface have the lowest mobility. Next, in order of increasing mobility, come the atoms in the abutments of several contact sections and in the apexes of the internal angles; the atoms at the boundaries of two contact sections and in the ribs of the internal angles; the atoms in the depressions of the surface; the atoms in the level sections of the surface; the atoms in the protuberances and elevations of the surface and in the ribs of external angles (it

being the case that the smaller the angle, the more mobile the atoms).

With the growing size of the crystals, as indicated in Table 43, the fraction of the mobile surface atoms is diminished (approximately, in an inverse ratio to linear dimensions). The fraction of the most mobile atoms in the ribs ("linear" atoms) and in the angle apexes ("punctate" atoms) is diminished even more rapidly. This fraction changes in an inverse ratio to the square (almost) and to the cube of the linear dimensions of the crystal.

[See next page for Table 42]

Footnote. The numbers in the last column of the above table can be accepted in first approximation as the values of the energy of activation Q in conditional units (see Paragraph 54).

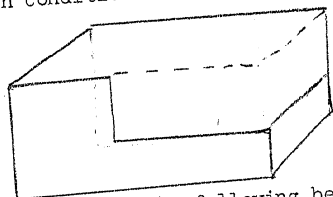


Figure 84. Referring to Table 43 following below:

1. atom inside crystal; 2. in apex of internal angle; 3. in rib of internal angle; 4. in the crystal surface; 5. in the rib of the external angle; 6. in the apex of the external angle.

TABLE 42

The Number of Neighboring Atoms Surrounding the Atoms in Various Parts of a Crystal with a
a Simple Cube Lattice (See Figure 8a)

No. in sequence	Location of atoms	Number of neighboring atoms		Energy of the bond with neighbor- ing atoms in conditional units	
		At distance equal to the parameter of lattice [1]	At distance less than double parameter of lattice [2]	At distance equal to the parameter of lattice [3]	At distance less than double parameter of lattice [4]
1	Inside crystal or inside the contact surface of two simi- larly orientated crystals	6	26	100	100
2	In apexes of internal angles or at the point of contact of 3 similarly orientated crystals	6	25	100	97.7
3	In the ribs of internal angles [continued]				

TABLE 42 [continued]

No. in sequence	Location of atoms	[1]	[2]	[3]	[4]
	or at the contact surface boundary of two similarly orientated crystals	6	23	100	92
4	On the surface of crystal	5	17	83.3	70.5
5	In the ribs of external angles	4	11	66.7	49
6	In the apexes of external angles	3	7	50	33

TABLE 43

The Relative Number of Different Atoms in Relation to the Dimensions of a Crystal with a
Simple Cube Lattice

Number of atoms in rib of cube	Total number of atoms	% of surface atoms w/rela- tion to total number of atoms	% of atoms in ribs		% of atoms in angle apexes	
			of all atoms	of atoms in the surface	of all atoms	of atoms in the surface
	8	100	100	100	100	100
2	10 ³	48.8	10.4	21.5	0.8	1.6
10	10 ⁶	5.9	0.12	2	$0.8 \cdot 10^{-3}$	$1.4 \cdot 10^{-2}$
100	10 ⁹	0.6	$0.12 \cdot 10^{-2}$	0.2	$0.8 \cdot 10^{-6}$	$1.3 \cdot 10^{-4}$
1000	10 ¹²	0.06	$0.12 \cdot 10^{-4}$	0.02	$0.8 \cdot 10^{-9}$	$1.3 \cdot 10^{-6}$
10000	10 ¹⁵	0.006	$0.12 \cdot 10^{-6}$	0.002	$0.8 \cdot 10^{-12}$	$1.3 \cdot 10^{-8}$
100000						

The fraction of the surface atoms, as related to the entire volume of the crystal, and the number of linear atoms (in the ribs), as related to the total number of surface atoms, becomes insignificant when the rib is 1,000 to 100,000 atoms long, which corresponds approximately to a length of 0.3 to 30 microns. However, due to numerous irregularities in the surface, the number of surface and linear atoms is actually greatly in excess of the number computed under the assumption of a regular geometrical shape.

A series of phenomena can be understood in the light of the mobility of the atoms (molecules) of solid bodies.

Pavlov^(50, 24), for instance, established that the melting point of a material drops with the degree of dispersion of its particles. According to Pavlov, particles having a diameter of 2 microns were melting at 7 degrees Centigrade below the particles with a diameter of 0.5 to 2 millimeters in the case of phenyl salicylate (salol), at 5 to 7 degrees below in the case of antipyrine, at 4 degrees below in the case of phenacetin. In all probability, the temperature of transition into a liquid state of the greater mobility atoms in the surface and, particularly, in the ribs and in the angle apexes, drops even to a greater extent. The supercooling of liquids in solidification also testifies to a lower melting point for surface atoms. It is long since known that evaporation of the surface layers of a liquid sets in at a point considerably below the boiling point, only upon the attaining of which the internal layers of the liquid begin to evaporate. To all appearances, the melting point of a solid body also corresponds to the temperature of the transition of the internal sections of the

crystal into a liquid state, and the transition into a liquid state of the surface layers occurs at considerably lower temperatures.

The phenomena of recrystallization are also easily understood in the light of the mobility of the atoms (see Paragraph 56).

Kuznetsov and Saratovkin⁽³⁸⁾ were altogether correct in ascribing the higher intensity of dissolution of dispersion crystals to the considerable number of atoms in the crystal ribs and in the angle apexes. Many researchers contend that with the increase in the degree of dispersion not only the rate of dissolution, but even the solubility of the substance is increased. Thus, Hulett⁽¹⁰³⁾ discovered that the solubility of gypsum with particles over 3μ in size was 15.3 millimoles per liter, and with the size of the particles 0.3μ it was 18.2 millimoles per liter. In the case of barium sulfate with 1.8μ -particles, solubility was 2.3 millimoles, and for 1.1μ it was 4.15 millimoles. Similar results were obtained with different materials by Ostwald, Stass, Glovzhinskiy, Jones, and Partington⁽¹⁰⁸⁾, and many other researchers⁽²⁴⁾. By the same token, the atoms in the ribs, apexes, and protuberances of the crystal should evaporate more intensively than the atoms in the depressions.

The decrease in the mobility of the atoms (molecules) located in the surface depressions of bodies may be illustrated by the considerable rise in the boiling points of liquids enclosed in capillaries. In very thin capillaries, the boiling point of water may be in excess of 200° Centigrade.

Finally, the changes in mechanical properties with temperature may also serve as proof of the variation in the mobility of atoms. The strength and hardness of metals at high temperatures is determined by the properties of the surface layers of the grains with the most loosely bonded atoms having a maximum degree of mobility, since the strength of a chain is the strength of its weakest link. While the moduli of elasticity are volumetric properties and are determined by the more numerous and less mobile internal atoms. Conformantly, as was already indicated, the strength and hardness in heating are reduced by several times ten, and the moduli of elasticity by several times only (see Figures 81 and 82).

The shifting of the atoms, in conformity with the second law of thermodynamics, must occur predominantly in such directions as to reduce the free energy of the system. Hence, with a rise in temperature, the amount of the residual stresses and the magnitude of the specific surface of the particles are diminished, and the contact between the particles grows. The mechanics of this phenomena will be analyzed in this chapter.

At absolute zero (-273° Centigrade) the mobility of the atoms in all metals equals zero. Correspondingly, when the melting point is attained, the mobility of the atoms in all metals also attains a respectively similar level, at which the crystal lattice is disintegrated. Ludwik was the first to introduce the concept of the so-called respective temperatures for various metals, i.e., temperatures that amount to the same fraction as related to the absolute melting point. It is probable that equal

respective temperatures are linked to equal atomic mobility and state of metals. Thus, Bochvar⁽¹⁴⁾ established that the recrystallization of different pure metals begins at respectively equal temperatures (30 to 40 percent from the absolute melting point).

54. Further Data on the Mobility of the Atoms

In most cases, the particles of metal powders and the grains of compact metals have linear dimensions on the order of 100,000 atoms (about 30 microns). Table 43 above shows that, in this case, there are only 6 surface atoms to 100,000 atoms inside the crystal. The number of linear and angular atoms is still smaller (12 to 10,000,000,000; and 8 to 10^{15}). The fraction of the most mobile surface, linear, and angular atoms, is insignificant, even if account is taken of the fact that, due to the irregularities of the particle surfaces and grains, the actual number of these atoms is tens and hundreds of times greater than indicated in Table 43.

Nevertheless, the behavior and the properties of metals at high temperatures are to a considerable extent determined specifically by these atoms with maximum mobility. This is due to the fact their insignificant amount is compensated by mobility, which is tremendous by comparison with the mobility of atoms inside the crystal.

With a rise in temperature, as already indicated in Paragraph 53, the oscillation range of the atoms is increased. Hence, with a rise in temperature, the location of the atoms in the lattice becomes less stable, and the number of atoms shifting from one junc-

tion of the lattice of the same or another crystal. As a measure of the mobility of the atom, it is most convenient to select the velocity of its displacement from a predetermined point of equilibrium.

According to Frenkel' (65), the mean period of time τ , during which the atom remains in bond with the same point of equilibrium, is expressed by formula

$$\tau = \tau_0 e^{\frac{Q}{RT}} = \tau_0 e^{\frac{Q}{RT}}, \quad (54/1)$$

where τ_0 is the oscillation period of the atom;

e is the base of natural logarithms;

Q is the energy of activation in calories per one atom, requisite for the displacement of the atom from a predetermined point of equilibrium;

Q is the same energy of activation in calories per gram-atom;

k is Boltzmann's constant;

R is the gas constant (almost equal to 2 calories per gram-atom per degree);

T is the absolute temperature

The mean "velocity" (mobility), at which the atom abandons a predetermined point of equilibrium, will be expressed by formula:

$$v = \frac{1}{\tau_0} e^{-\frac{Q}{RT}} = a e^{-\frac{Q}{RT}} \quad (54/2)$$

where

$$a = \frac{1}{\tau_0} = \text{const.}$$

The number of atoms n of a given category (such as linear, or atoms inside the crystals), abandoning in a unit of time the point of equilibrium in some volume of metal, is determined by formula:

$$n = Nv = Na e^{-\frac{Q}{RT}}, \quad (54/3)$$

where

N is the number of all atoms of the given type in the given metal volume;

Q is the energy of activation for the atoms of the given type;

A has approximately the same value for atoms of any type.

The energy of activation Q varies with the location of the metal atoms. It is determined by the magnitude of the forces of bond with other atoms, which must be broken in order to effect the displacement of the atom from the given point of equilibrium. In the last two columns of Table 42, in Paragraph 53, are given the computations (in conditional units) of the energy of the bond of differently-located atoms with their immediate neighbors (in the penultimate column, with atoms at a distance of one parameter, and in the last column, atoms at a distance of less than two parameters from the lattice).

Footnote. It was assumed that the atomic bond energy runs in an inverse ratio to distance.

Table 42 shows that, in the case of the angular atoms, this energy is two and three times below that for the atoms inside the crystal.

Footnote. These differences in the amount of energy for different categories of atoms increase with the increase in the computation distance of the forces of interaction between the atoms. It is, therefore, possible that the values of Q , computed by Table 42 for the greater mobility atoms, are somewhat high.

From now on, for a rough computation of the energy of activation for different atoms, we will assume the values of Q as being in direct ratio to the bond energy in the last column of Table 42 (i.e., for atoms inside the crystal, $Q = 100$ percent; for atoms in the internal angle apexes, $Q_{BH} = 97.7$ percent; for atoms in the smooth free surface, $Q_{\Pi} = 70.5$ percent; for atoms in the internal angle ribs, $Q_{BHP} = 92$ percent; for the linear atoms in the external angle ribs, $Q_{\Gamma} = 49$ percent; and for the atoms in the external angle apexes, $Q_{\gamma} = 33$ percent). For the atoms not in the free but in the contact sections of the particle surfaces (and also at the boundaries of the grains in compact metals), in the presence of a different orientation of the osculating crystals, the forces of bond are greater than on the free surface, but less than inside the crystal. Hence, if the activation energy of the atoms inside the contact surface is designated $Q_{K\Pi}$, in the ribs of the contact surface -- $Q_{K\Gamma}$, and in the apexes of the contact surface -- $Q_{K\gamma}$, then:

$$Q_{K\gamma} < Q_{K\Gamma} < Q_{K\Pi} < Q; Q_{K\Gamma} > Q_{\Gamma}; Q_{K\Pi} > Q_{\Pi}$$

Let us examine a conglomerate of crystals, in which there are N_1 atoms of lesser mobility with an activation energy Q_1 and mobility v_1 and N_2 atoms of greater mobility with an activation energy Q_2 , and mobility v_2 ($N_1 > N_2$; $Q_1 > Q_2$; $v_1 < v_2$). The ratio of the mobilities $\frac{v_2}{v_1}$, in conformity with formula (54/2), will be (assuming that τ_0 is the same for both categories of atoms):

$$\frac{v_1}{v_2} = e^{\frac{Q_1 - Q_2}{RT}} \quad (54/4)$$

Let us designate the number of the less mobile atoms, displaced in a unit of time, by w_1 , and the number of atoms of higher mobility by w_2 .

The ratio $\frac{w_2}{w_1}$, in conformity with formulas (54/3) and (54/4), equals:

$$\frac{w_2}{w_1} = \frac{N_2 v_2}{N_1 v_1} = \frac{N_2}{N_1} e^{\frac{Q_1 - Q_2}{RT}}, \quad (54/5)$$

If the ratio $\frac{w_2}{w_1} < 1$, the behavior and properties of the metal are determined, principally, by the more numerous atoms of lesser mobility. If the ratio $\frac{w_2}{w_1} > 1$, then, provided the absolute magnitude of w_2 is adequately great, the behavior and the properties of the metal may be primarily determined by the less numerous atoms of greater mobility. At low temperatures, the ratio $\frac{w_2}{w_1}$ is considerably greater than unity, but the magnitude of w_2 is so small, that the few atoms of great mobility exert no effect upon the behavior and the properties of the metal.

According to Langmuir⁽¹²⁰⁾, the energy of activation per gram-atom, in the case of diffusion of thorium into tungsten, was equal to 120,000 cal (100 percent); for diffusion over the con-

tact surface (along the boundaries of the grains) -- 90,000 cal (75 percent); and for diffusion over the free surface, 66,400 cal (55.3 percent). Substituting the corresponding values into formula (54/4), we derive that, at 1800° K (1523° Centigrade), the mobility of the thorium atoms inside the tungsten crystal was 4,000 times less than in the contact surface, and 3,000,000 less than in the free surface.

The values of the activation energy of the metal atoms inside the crystal must coincide approximately with its latent heat of evaporation. In accordance with the data contained in the Landolt-Bernstein tabulations (119), the latent heat of evaporation for copper is 70,600 calories per gram-atom. Let us accept this amount of heat as the value of the activation energy of the copper atoms inside the crystal. The activation energy of the copper atoms in the contact surface (the activation energy during the recrystallization of copper) as per Cook and Richards⁽⁸⁶⁾, is 66,000 calories, in the presence of little deformation and coarse grain of the metal, and 44,000 calories in the presence of considerable deformation and fine initial grain. The above upper value of this energy differs little from the latent heat of evaporation for copper, while the lower value departs from it considerably. Anderson and Mehl⁽⁷⁷⁾ established the activation energy of aluminum atoms (the energy of activating the growth of the grain of compact aluminum) to be 61,500 calories, at 1.6 percent elongation, and 51,500 calories at 20 percent elongation. Such a difference in the activation energy, in the presence of different degrees of deformation, is due to the following. In the contact surface (surface of the grain) there are lower

mobility atoms (inside the surface) as well as higher mobility atoms (angular atoms and those on the surface of voids). If in a unit of time, as per formula (54/3), N_1 atoms of lesser mobility with an activation energy Q_1 , and N_2 atoms of greater mobility with an activation energy Q_2 ($Q_2 < Q_1$), abandon the point of equilibrium, the observed activation energy Q_H is determined by formula

$$Q_H = \frac{n_1 Q_1 + n_2 Q_2}{n_1 + n_2} \quad (54/6)$$

With an increase in the degree of deformation, the number of atoms of greater mobility (n_2) is increased, and the activation energy, therefore, is reduced (approximating, within the limit, Q_2 , in the presence of the upper limit, Q_1).

The activation energy of the copper atoms in the free surface, computed by the growth in the rate of shrinkage of the copper powder with the increase in the baking temperature, ranges from 25,000 to 40,000 calories per gram-atom. The lesser value of this energy range practically coincides with the activation energy of the angular atoms Q_y , computed in conformity with Table 42 ($Q_y = 70,600 \times \frac{33}{100} = 23,300$ calories). The upper value of the range (40,000 calories) is greater than the activation energy of the linear atoms, Q_L ($Q_L = 70,600 \times 49/100 = 34,600$ calories), but is less than the activation energy of the surface atoms Q_H ($Q_H = 70,600 \times (70.5/100) \approx 49,800$ calories). Substituting in formula (54/4) the respective experimental values for Q (25,000; 40,000; 70,600 calories), we derive that, at 300° K (room temperature 27° Centigrade), the mobility of the copper atoms in the free

surface is 10^{21} to 10^{36} times, at 500°K ($223^\circ \text{Centigrade}$) 10^{-13} to 10^{22} times, at 1000°K ($727^\circ \text{Centigrade}$) it is 4 million to 100 billion times, and near the melting point at 1350°K ($1077^\circ \text{Centigrade}$) it is 80,000 to 100 million times greater than the mobility of the copper atoms inside the crystal.

Let us bake some powdered copper in the case of which the ratio of low-mobility atoms inside the particles to the high-mobility atoms in the free surface $\frac{N_1}{N_2} = 10,000$ (such a ratio actually exists only in the case of very coarse powders, for fine powders it is lower). Substituting in formula (54/5) this ratio and the above indicated lesser values $\frac{v_2}{v_1}$, we derive that ratio $\frac{n_2}{n_1}$ at $727^\circ \text{Centigrade}$ equals 400, and at $1077^\circ \text{Centigrade}$ it equals 8. Hence, the behavior of powdered copper in baking is determined by the surface atoms, and, only in the case of very coarse copper, at temperatures near the melting point, the mobility of the atoms inside the particles, also has a perceptible effect upon the baking process.

Let us analyze the deformation at various temperatures of compact polycrystalline copper. The atoms in the surface of the grains (contact surface) have a higher activation energy and a lower mobility than the atoms in the free surface of the particles. Hence, the ratio $\frac{n_2}{n_1}$ in formula (54/5) becomes less than unity long before the melting point is attained. At room temperature, the mobility of the atoms is so low that it has no significance. In heating, the mobility of the atoms affects deformation, by inducing the phenomena of creep (see Paragraph 59). When the temperatures are not too high, $\frac{n_2}{n_1} > 1$, and the creep is determined

primarily by the atoms in the grain surfaces. With a further rise in temperature, the ratio $\frac{n_2}{n_1}$ may become less than unity, and the metal will flow in a manner similar to the flow of viscous liquids and amorphous bodies (pitch, glass).

Thus, although the number of surface atoms is negligible, their effect upon the behavior of metals at high temperatures is very great. This effect is further increased as a result of recrystallization. If, for instance in heating, the linear dimensions of the grain increased twice, it means that, in annealing almost all the atoms of the metal (no less than 87 percent) during a certain time interval were located at the boundaries of the grains.

With a rise in temperature, the relative mobility of the metal atoms increases, at first very rapidly, then at a slower rate. In the case of a temperature rise by 100 degrees, from 300 to 400° K (from 27 to 127° Centigrade), the mobility of the angular atoms of copper is increased 16,000 times; the mobility of the linear atoms, 18 million times; the mobility of the surface atoms, 850 million times; the mobility of the atoms inside the crystal, 10^{21} times. With a 100° rise from 1000 to 1100° K (from 727 to 827° Centigrade), the mobility of the angular atoms is increased three times; the mobility of the linear atoms, 4.8 times; the mobility of the surface atoms, 9.5 times; and the mobility of the atoms inside the crystal, 23 times.

Footnote. The mobility values are computed by the values of energy activations as based on Table 42.

The mobility of the surface layer of atoms is so great that Volmer⁽¹⁵³⁾ considers it to be a semiliquid substance and Frenkel⁽⁶⁵⁾ believes it is an adsorbed gas. The difference in the activation energy of the atoms disposed at different places in the surface and inside the copper crystal lies within the range of 20,000 to 47,000 calories per gram-atom. It is considerably greater than the amount of heat required to melt copper (which is 3200 calories).

Let, at some temperature T_y , the mobility of an angular atom be equal to the mobility of an atom inside the crystal at the temperature of melting. This equality can be expressed by formula:

$$ae^{-\frac{Q}{RT_m}} = ae^{-\frac{Q_y}{RT_y}}, \quad (54/7)$$

where Q is the activation energy of the atom inside the crystal;
 Q_y is the activation energy of the angular atom;
 T_m is the absolute melting point of the metal;
 T_y is the temperature "equivalent" to the melting point for the angular atom.

It follows from formula (54/7) that:

$$\frac{T_y}{T_m} = \frac{Q_y}{Q}. \quad (54/8)$$

This formula (54/8) and Table 42 make it possible to compute the equivalent temperatures of melting for the various atoms of the metal. They constitute 33 percent of the absolute melting point, in the case of the angular atoms; 70.5 percent in the case of the surface atoms (these values are rather underestimates than overestimates). It is possible that the temperature threshold of

recrystallization, which, according to Bochvar, is 30 to 40 percent of the melting point, is due to the "liquefaction" of the angular and linear atoms. The generally accepted baking temperature (equal to the temperature of recrystallization of the powder metal -- about 70 percent of the melting point) can also be explained by the transition of the surface layer of particles into a liquid state.

55. Deformation of Compact Metals Stipulated by the Mobility of the

Atoms

The movement of atoms occurring in the process of heating is unavoidably tied in with various types of deformation. By the type of the displacement of the atoms, these deformations can be divided into reversible and non-reversible. By the volume of the structural elements, with which the deformations are tied in, they can be classified into three categories:

(1). Deformation of crystalline lattice, the growth of its parameters with heating, and their diminution with cooling, the reconstruction of the lattice type (for instance, the $\alpha \rightarrow \gamma$ transformation in iron). This type of deformation, in the case of compact metal, can be practically considered as reversible, i.e., that, in cooling, the heated metal will revert to its initial state.

(2). Deformation of the crystallites, which is manifested in the non-reversible displacement of the atoms from some of the crystalline lattice junctions onto others. The displacement may occur inside the individual crystallites, as well as from some crystallites onto others. This deformation is non-reversible, and the disposition

of atoms, attained during the heating process, remains after cooling. The removal of lattice distortions and residual stresses, induced by the effect of cold-hardening, is also linked to the deformation of the crystallites.

(3). Deformation of the crystallite conglomerate. The non-reversible displacement of the atoms is usually tied in not only with the deformation of the crystallites, but also with their reciprocal displacement, resulting in the non-reversible deformation of the conglomerate of crystallites throughout the entire volume (change in porosity, buckling).

The heating of metals to temperatures approximately 20 percent from their absolute melting point is linked only to the reversible deformations of the lattice and the body subjected to heating (expansion in heating, shrinkage in cooling).

At higher temperatures, the increased mobility of the atoms, in addition to the reversible deformations of the lattice and volume, results in non-reversible changes of properties (regression or repose), of magnitude and form of structural elements caused by surface tension), of the form and volume of the entire body (buckling, a change in the state of the surface, a change in density).

56. Regression and Recrystallization in Compact Metals

The cold deformation in compact metals is tied in with the accumulation of excess energy (equal to the work expended for non-reversible deformation), the formation of residual stresses, the increase in strength and hardness. With regards to this, compact

side the individual grains. It is these displacements that result, during regression, in the removal of lattice distortions, in the absorption of residual stresses, in detoughening, in the increase of plasticity, and in the liberation of the energy of cold deformation. Some phenomena, in the opinion of the author, also testify to an increase, during regression, of the intergranular contact (the increase in electrical conductivity). The temperature of the beginning of regression is diminished considerably with the growth in the degree of deformation. In the opinion of the author, the latter is linked primarily to the increase in the number of the maximum-mobility atoms as a result of the reduction in size of the grain during the cold deformation (Paragraph 53, Table 43). Thus, if the grain is reduced in size ten times, the number of the maximum-mobility atoms is increased: in the surface, 10 times; in the ribs, 100 times; and in the angle apexes, 1000 times.

At still higher temperatures (as established by Bochvar^(14,16) for pure metals within 30 -- 40 percent of their absolute melting point), the mobility of the atoms is increased to such a degree that they pass from one crystallite into another. This process is known as recrystallization. Recrystallization is linked to the final removal of residual stresses (final detoughening) and to the growth of the grain. The laws of recrystallization of compact metals are basically reduced to the following.

(1). The temperature of the beginning of recrystallization is diminished with the increase in the degree of deformation. In the opinion of the author, this is primarily linked to the increase

in the number of mobile atoms as a result of the reduction in the size of the grain during the cold deformation.

(2). The temperature of the beginning of recrystallization is diminished with the size of the grain. Thus, Cook and Richards⁽⁸⁶⁾ established that the recrystallization of pure copper with a grain size after deformation of less than 0.8 micron was beginning already at room temperature equal to 22 percent of the absolute melting point.

(3). The size of the grain after recrystallization, at predetermined temperature and time-lag, is diminished with the degree of deformation.

(4). The rate of the isothermic growth of the grain with time is rapidly diminished and drops practically to zero already after a time-lag of several hours.

(5). With the increase in temperature, the rate of growth and the ultimate size of the grain are increased.

Let us analyze the contact between a small and a large grain (Figure 85). Although the number of surface atoms in contact is exactly the same in both the large and the small grain, the number of higher mobility atoms in the ribs and in the angle apexes, is much greater in the small grain. Therefore, a greater number of atoms will pass from the small grain into the large one in a unit of time than the other way around, at the expense of the difference in the number of the maximum-mobility linear and angular atoms and the differences in mobility as between these active atoms and the remainder of the surface atoms.

This opinion can be substantiated by the findings of Tammann⁽⁶⁰⁾. In order to obtain confirmation of the correctness of his theory on the braking effect of admixtures, Tammann studied the kinetics of the growth of grain. His experiments showed that the number of grains n per area unit of the microslide was varying with the time of annealing z , or conformantly with an equilateral hyperbola:

$$\frac{1}{n} = \frac{z}{k} \quad (56/1)$$

where k = constant,

or conformantly with a non-equilateral hyperbola

$$\frac{1}{n} = \frac{z}{k+bz} \quad (56/2)$$

where k and b are constants.

The number of grains runs in an inverse ratio to their cross section, in other words, to the square of the linear value l^2 , so that $l^2 = \frac{1}{n}$. Substituting into formulas (56/1) and (56/2), the above value $\frac{1}{n}$, we derive in the case of the equilateral hyperbola:

$$l^2 = \frac{z}{k} \quad (56/3)$$

and for the non-equilateral hyperbola:

$$l^2 = \frac{z}{k+bz} \quad (56/4)$$

By differentiating formula (56/3), we derive:

$$\frac{dl}{dz} = \frac{1}{2kl} = \frac{\text{const.}}{l} \quad (56/5)$$

The expression $\frac{dl}{dz}$ in formula (56/5) is the momentary linear rate of growth of the grain. Thus, in a number of cases, the rate of growth $\frac{dl}{dz}$ runs in an inverse ratio to the mean linear size of grains.

But the rate of growth is determined not by all the surface atoms, but by the most active ones -- linear and angular, and, first of all, by the most numerous -- the linear atoms. In the simplest case, the rate of the linear growth of the grain runs in direct ratio to the square root of a fraction, the numerator of which is the number of linear atoms, and the denominator is the number of all atoms. In other words, the rate of the linear growth of the grain runs in a direct ratio to the number of linear atoms with relation to the surface atoms, and in an inverse ratio to the linear dimensions of the grain l (see Paragraph 53, Table 43), i.e.,

$$\frac{dl}{dz} = \frac{\text{const}}{l}.$$

Thus, we derived theoretically, for the rate of growth of the grain, the same formula (56/5), which Tammann computed empirically.

In most cases, the rate of growth diminishes even more rapidly with time (partly because of the more rapid decrease in the number of angular atoms, in an inverse ratio to the square, and not to the first power of the linear dimensions; partly because of the diminution in the roughness of the surface and the drop in the contrast of the grain size during growth, which also induces a reduction in the number of active atoms -- at a more rapid rate than

with the first power of l . In these cases, the rate of growth can be characterized by formula

$$\frac{dl}{dz} = \frac{\text{const}}{l} \cdot \frac{1}{F(z)}, \quad (56/6)$$

where $F(z)$ is some function of time increasing with the time-lag.

Upon differentiating the Tammann formula for a non-equilateral hyperbola (56/4), we derive:

$$\frac{dl}{dz} = \frac{\text{const}}{l} \cdot \frac{1}{(k+bz)^2}, \quad (56/7)$$

i.e., an expression of the type of formula (56/6). Thus, even in this case, the author's theory is confirmed by the Tammann data.

Footnote. During the initial stage of recrystallization, when the few grains, the so-called centers, or nuclei, grow at the expense of the balance of the mass of grain fragments, the rate of growth, as shown by recent works (77, 145), is practically constant. The theoretical computation in this case, as based on Table 43, also results in a practically constant rate of growth. (For example, if, at the beginning, the nucleus was ten times larger than the other grain fragments, and then grew in size 100,000 times, while the size of the grain fragments remained the same, the rate of growth of the nucleus is increased only 1.1 times, i.e., remains practically unchanged).

It follows from formula (56/6) that, at some predetermined size of the grain, the rate of its isothermic growth becomes very insignificant, and practically is discontinued regardless of interparticle admixtures. With higher temperatures, mobility, i.e., the rate of migration of active atoms, is increased.

In recrystallization, it is not always the case that the larger grains are increased in size at the expense of the smaller ones, as growth also depends on the orientation of the crystallites. Differences in orientation are, in the final analysis, reduced to differences in the mobility of the atoms. Let the boundary of a crystal with a simple square lattice pass at an angle φ ($\varphi \leq 45^\circ$) to the side of the square. According to Jamada (156) and Frenkel' (65), such a boundary can be visualized as a ladder, with the height of the rungs equal to the parameter of lattice a , and its mean length equal to $a \cot \varphi$ (Figure 86).



Figure 86. Boundary between differently orientated crystals

The ratio of the number of the higher-mobility atoms in the external angles of the rungs to the lower-mobility atoms along the length of the rungs, for such a boundary, equals $\tan \varphi$. Let such a crystal A abut with a crystal B, for which the boundary line passes along the side of the square (the angle between the boundary and the side $\varphi = 0$). At the boundary, from the side of crystal B, there are more low-mobility atoms, and from the side of crystal A, there are more high-mobility atoms. Hence, more atoms will migrate from A to B, per unit of time, than in the opposite direction, and B will grow at the expense of A. During this growth, the value of the angle φ does not remain constant. Since A loses more high-mobility than slow-mobility atoms, the ratio of the number of high mobility to the number of low-mobility atoms, which is equal to $\tan \varphi$, is rapidly diminished. On the contrary, in

crystal B, this ratio is increased. Therefore, angle ϕ between the boundary and the side of the square of crystal A is rapidly diminished, and angle ϕ' between the boundary and the side of crystal B is increased and the growth of B at the expense of A is retarded. The final discontinuation of growth at the expense of differences in orientation, will occur when the boundary becomes established at a neutral angle, equal to $\phi/2$ (the dotted line in Figure 86). Any further growth (B at the expense of A or vice versa), is only possible at the expense of differences in the size of the grain.

In the case of powdered metals, the change in the orientation of the boundaries between the particles, as a rule, precedes the visible growth of the grain. Harker and Parker (99) established that, during the recrystallization of compact metals, the magnitude of the angles between the grain facets changes, approaching in its limit, the value of 120° .

In the process of growth, the boundaries of the grains are continuously being displaced. In the process, the higher-mobility surface atoms, getting into the internal layers, lose their mobility, and the low-mobility internal atoms, finding themselves at a new boundary, on the contrary, attain higher mobility, etc. Thus, all the time there is the process of exchange of mobility, exchange of fluidity. In other words, as if there were taking place a continuous process of solidification of some and liquefaction of other atoms. In the final analysis, this process results in a reduction of the number of high-mobility surface atoms with greater kinetic energy, and to a liberation of energy in the form of the "latent heat of mobility diminution". The liberation of energy during recrystal-

lization was established by Sato (55).

At low temperatures, 99.99 percent of the atoms are in the internal layers, and they are not drawn into the process of fluidity exchange, playing the part of a sort of "inactive fund". With an increase in temperature, recrystallization transforms this "dead fund" into "working fund".

For instance, with a two-time increase in the linear dimensions of the grain, at least $100(1 - \frac{1}{2^3}) = 87.5$ percent of all the atoms are drawn into the fluidity exchange, with a three-time increase in grain diameter, 96.3 percent of all the atoms are drawn in.

57. Deformation Induced by the Movement of Atoms along the Surface

Recrystallization is linked to the displacement of atoms from one crystallite into another, perpendicular to the surface of the grain. The atoms can also become displaced along the surface of the crystallites, which is connected with changes in the form of the grains and the entire metal.

Tammann established that, at temperatures close to the setting in of recrystallization, the surface of burnished plates becomes rough. The angle, at which the sliding of two thoroughly burnished metal plates begins, as indicated by Tammann and Salge⁽¹⁵⁰⁾, is increased considerably after heating approximately to the temperature of recrystallization. These changes are due to the non-reversible displacement of atoms, in heating, along the surface of the metal.

Table 44 is a compilation of temperatures at which the non-reversible displacement of atoms occurs.

TABLE 44

The Temperature of the Beginning of Displacement of
Atoms, as per Tammann, in Degrees Centigrade

	<u>Cu</u>	<u>Fe</u>	<u>Ni</u>
Temperature at which angle of slip between burnished plates increases	160	170	200
Temperature at which tubercles appear on bur- nished surface	200	220	220
Temperature at which the displacement of the grain boundaries begins	200	350	530

As seen from Table 44, surface deformation begins at lower temperatures than the growth of the grain. Tammann considers this phenomenon to be due entirely to the low sensitivity of the methods of determination of the displacement of the grain boundaries. However, in the opinion of the author, the displacement of atoms along the free surface of the metal begins at lower temperatures than the displacement of atoms athwart the contact sections of the surface of the grains, since the atoms in the open sections of the surface have greater mobility than in the contact sections (see Paragraph 54).

When thin metal leaves are heated, the displacement of the atoms causes buckling. The rate of buckling is rapidly increased with temperature, due to the increased mobility of the atoms.

This phenomenon was utilized by Tammann and Boehme (147), and also Savai (133) for the determination of surface tension in hard metals. A tension load was applied to the plate. With the value of the load equal double the surface tension, buckling stopped.

The temperature, at which buckling sets in, increases rapidly with the thickness of the metal leaf. In tests with gold leaflets, conducted by Tammann and Savai, it was oscillating between somewhat over 200° Centigrade for a thickness of 0.1 micron and 600 to 800° Centigrade for a thickness of 0.8 micron. Such a drop in the temperature of buckling with a reduction in the leaf thickness is due to the growth in the number of the greater mobility surface atoms. A more formal explanation of this phenomenon is given by Tammann and Boehme. With temperature, the strength of the metal drops more rapidly than its surface tension. The strength of the metal is greater in the thicker leaf, while the value of surface tension is the same. Hence, equilibrium between strength and surface tension, in the case of a thick leaf, is established at higher temperatures.

Such phenomena as the transition in annealing of lamellar perlite into granular, are also due to an increase in the mobility of the atoms and to the effect of surface tension.

58. Volumetric Changes During the Annealing of Compact Metals

Table 45 below cites the data by Kal'baum and Sturm (60) on the change in density as a result of annealing platinum wire.

TABLE 45

Change in Density Following the Annealing of
Platinum Wire (as per Kal'baum and Sturm)

	<u>1</u>	<u>2</u>	<u>3</u>
Platinum wire cold-drawn to			
a diameter of 1 millimeter	21.4136	21.4226	21.4233
Same as above after anneal-			
ing for 3 minutes	21.4134	21.4323	21.4324
Platinum wire cold-drawn to	21.4181	21.4157	---
a diameter of 0.7 millimeters			
Same as above after anneal-			
ing for 3 minutes	21.4314	21.4315	21.4332
Platinum wire cold-drawn to			
a diameter of 0.4 millimeter	21.4142	21.4147	21.4134
Same as above white-heated			
for 3 minutes	21.4308	21.4310	21.4317

It follows from Table 45 that the porosity of compact metals is reduced in annealing. The diminution in porosity as a result of heating was also noted in the works of Tammann and Bredemeyer (148) and others.

59. Deformation in Heating under the Effect of External Forces --

Creep in Metals

Heretofore we discussed the deformation of heated metals

under the effect of internal interatomic forces. However, the growth in the mobility of the atoms in heating also manifests itself in deformation induced by external forces.

The aggregate of phenomena observed in deformation (particularly slow deformation) of metals under the effect of external stresses, at temperatures conducive to the perceptible mobility of the atoms, has come to be known as creep (this paragraph discusses only deformation through tension). The basic characteristics of such deformation can be reduced to the following.

(1). Under the effect of predetermined external load, the metal at first sustains a momentary elastic or elastic and plastic deformation. Then, a protracted continuous flow (creep) of the metal sets in. The rate of creep in the first stage is first diminished, then sustained for some time at a continuous minimum level, and, finally, it may increase. Given an adequate magnitude of load and rate of creep, the latter may result after a more or less protracted period by the rupture of the metal.

(2). The rate of creep is rapidly increased with temperature and load. This acceleration is particularly pronounced during the temperature of recrystallization.

(3). The force required to obtain a predetermined degree of deformation is increased with the rate of deformation.

(4). With rapid deformation and low temperatures, the formation of planes of slide and considerable grain deformation is observed. For slow deformation and high temperatures, the absence of sliding

and of perceptible deformation of grains, which retain equiaxiality, is characteristic.

(5). With rapid deformation and low temperatures, intracrystalline fracturing is observed. Slow deformation at high temperatures, on the contrary, is linked to intercrystal line fracturing. The temperature of the transition from one type of fracturing to the other is known as the temperature of equal cohesion, i.e., of equal intra- and inter-crystal-line strength), and it usually coincides with the minimum temperature of recrystallization.

(6). The deformation of fine-grained metals at low temperatures and at rapid rates requires greater forces as compared to the deformation of coarse-grained metals. The reverse is true of deformation at high temperatures and slow rates.

(7). The cold deformation of a metal is strongly inhibited during the toughening of the metal. Preliminary cold-hardening, on the contrary, facilitates creep very perceptibly at temperatures above the temperature of equal cohesion.

For a better familiarization with the phenomena of creep, the author recommends the articles by Hanson⁽⁹⁷⁾, Kanter⁽¹¹²⁾, Clark and White⁽⁸⁵⁾, Becker, Hanfstengel and Hanemann⁽⁹⁵⁾, Greenwood and Warner⁽⁹³⁾, McKeown⁽¹²³⁾, Chalmers, Odling⁽⁴⁶⁾. The only available book "Creep in Metals" by Tepsel⁽⁶¹⁾ has been regrettably outdated.

The majority of the researchers believe that the non-reversible deformation in creep is stipulated to a considerable extent by the mobility of the atoms induced by the temperature effect. This phenomenon

enon of creep is greatly, though not completely, similar to the deformation flow of amorphous substances, such as glass, pitch, which essentially are liquids of very high viscosity.

If creep is induced by the mobility of the atoms, a very considerable fraction of deformation must be due to the displacement of the greatest mobility atoms in the surface of the grains. With constant temperature and load, the number of surface atoms displaced in a unit of time is obviously in direct ratio to the total number of atoms at the boundaries of the grains.

The participation in creep of the lower mobility internal atoms, in all probability, takes place as a result of the following processes:

- (1). Fluidity exchange with the surface atoms during the displacement of the grain boundaries. The number of atoms taking part in this process, at constant temperature and load, is in direct ratio to the total number of atoms at the grain boundaries.
- (2). Accelerated mobility of several atomic layers nearest to the surface of the grain (see Paragraph 56). The number of these atoms displaced in a unit of time must also be in direct ratio to the number of atoms at the grain boundaries.
- (3). The mobility of the internal atoms -- the number of these atoms is (precisely to within fractions of a percent) almost 100 percent of the total number of atoms (see Paragraph 54, Table 43). As a result of this process, the rate of deformation, at predetermined load and temperature, can be considered practically constant and not dependent upon the number of atoms at the boundaries of the grains.

In conformity with the above, at constant temperature and load:

$$\dot{V} = c_1 n_1 + c_2 n_2 \quad (59/1)$$

where $\dot{V}$ is the rate of creep;
 c_1 and c_2 are constant coefficients;
 n_1 is the number of internal atoms;
 n_2 is the number of atoms at the grain surfaces

Since n_1 (with a precision to fractions of a percent) is constant, and n_2 is in direct ratio to the size of the specific grain surface s , formula (59/1) may be written down as follows:

$$\dot{V} = \dot{V}_1 + k s \quad (59/2)$$

where $\dot{V}_1$ is a constant equal to the creep velocity component induced by the inherent mobility of the internal atoms, or, which is the same, the rate of creep in a monocrystal;
 k is a constant coefficient;
 s is the size of the specific grain surface.

Let us analyze the process of creep under constant temperature and load.

During the first stage of creep, the size of the specific grain surface s , in connection with the phenomena of recrystallization, must be reduced, at first rapidly, then slowly (see Paragraph 56). Therefore, in conformity with formula (59/2), the rate of creep must also be decreased.

Footnote. The process of reduction in the size of the specific surface proceeds even in the absence of the apparent growth of the grain. If the actual surface of the grain becomes reduced to seeming geometrical dimensions, no growth will be discernible, but the specific surface may be reduced by hundreds of times.

During the second stage of creep, the reduction in the size of the specific surface is discontinued, and its magnitude becomes practically constant (see Paragraph 56). Therefore, the rate of creep attains its minimum value and becomes practically constant, in conformity with formula $(59/2)$. During this stage of creep, the rate of deformation of specimens with various grain sizes increases linearly with the magnitude of the specific surface (which is inversely proportional to the grain diameter). Figure 87, which is a curve graph plotted by the author in accordance with the experimental data by McKeown⁽¹²³⁾, relating to lead with a varying size of grain, at room temperature and a load of 0.35 kilogram per square millimeter, shows a linear relationship as per formula $(59/2)$. Neither McKeown himself nor other researchers took note of this simple relationship. The rate of creep, extrapolated with the aid of the graph in Figure 87, to apply to a monocrystal, is approximately 16 times below that of a polycrystal with a grain size of 0.1 millimeter. Thus, the atoms at the grain boundaries may play a greater part in the phenomena of creep than the internal atoms. Under very high temperatures, the differences in mobility, as between various atoms, are leveled off (see Paragraph 53), it being the case that the term k_s in formula $(59/2)$ may be

disregarded, and the rate of deformation will not depend on the size of grain.

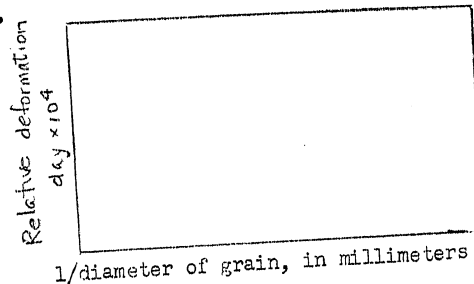


Figure 87. The ratio between the rate of creep and the specific surface (plotted by the author in accordance with the McKeown data)

During the third stage, the actual cross section of the specimen begins to diminish as a result of both shrinkage in deformation as well as formation of fissures, which for some reason or other are not filled fast enough with mobile atoms. These fissures develop in the weakest link of the chain, at the grain boundaries. Once started, this process progresses as a result of the increased load upon the remaining part of the cross section of the specimen, the rate of creep is accelerated, and the process may lead to the intercrystalline disintegration of the specimen.

The acceleration in the rate of creep in preliminary cold-hardened specimens is easily understood in the light of the increased mobility of the atoms as a result of toughening. It is probable that the preliminary cold treatment causes a considerable increase in the specific surface of the grains.

It was already pointed out in the previous text that the state of crystalline substances under temperatures of perceptible atomic mobility differs substantially from their state under low

temperatures. Heated crystalline bodies are considerably different from amorphous bodies, such as bitumen, asphalt, and glass, which essentially are liquids of high viscosity.

Amorphous substances are homogenous, and their atoms, in the main, have the same mobility, irrespective of location. Therefore, at a definite temperature, the rate of deformation V , i.e., the number of atoms displaced per unit of time, runs in direct ratio to the external stress, i.e.,

$$V = k \sigma \quad (59/3)$$

and

$$dV = k d\sigma \quad (59/4)$$

where k is a constant (at a given temperature) coefficient, equal to the fluidity of the material, it being the case that

$$k = \frac{1}{\varphi} = \text{const}, \quad (59/5)$$

where φ is the viscosity of the substance.

In contradistinction to amorphous bodies, crystalline bodies are heterogeneous and consist, theoretically speaking, of two "phases", a higher-mobility fluid phase and a lower-mobility non-fluid phase. The fluid phase is comprised by only a small part (fractions of a percent) of the material on the surface of the crystallite, where the higher mobility atoms are. It being the case that there is a continuous exchange of state between the fluid and non-fluid material. At low temperatures, the intensity

of this process is negligible, and the behavior of the metal is stipulated by its non-fluid part comprising 99.9 percent of the entire substance. At high temperatures, the above process is rather intensive, and the behavior of the metal is determined to a considerable extent by the properties of its fluid fraction which usually comprises less than 0.1 percent of the entire material. It may be said that, in crystalline bodies, at low temperatures, the negligible number of surface atoms constitutes a sort of revolving fund, while the remainder^{der} of the atoms is the inactive fund. At high temperatures, some indefinite part of the inactive fund is drawn into circulation. In amorphous substances the entire fund is a revolving fund.

A characteristic feature of heated metals, in contradistinction to amorphous substances, is the variable magnitude of fluidity in metals. At a predetermined temperature, the value of fluidity runs in relation to two factors:

- (1). The change in the number of the higher-mobility atoms at the grain boundaries.
- (2). The change in the intensity of drawing in the low-mobility atoms into the fluidity exchange process.

We have familiarized ourselves with the first of these factors. The number of the highest-mobility surface atoms is diminished with time. Hence, in isothermal heating, a diminution in the rates of recrystallization (see Paragraph 56) and creep is observed with a time-lag.

The second factor, the intensity of fluidity exchange,

depends greatly on the rate of creep, and consequently, on the load. Let us analyze in more detail this dependence for creep, under constant temperature and constant size of the specific grain surface (i.e., with constant number of atoms in the grain surface).

The process of creep is primarily a result of displacement of the maximum-mobility atoms in the surface of the grains. This displacement may basically follow two routes. In the first case, the surface atoms are passing from grain to grain, it being the case that some number of the surface atoms penetrate inside the grains and lose their mobility, with exactly the same number of internal atoms finding their way to the surface and attaining mobility. Thus, the intensity of this mobility exchange runs in direct ratio to the rate of displacement of the atoms, i.e., to the rate of creep $\sqrt{\quad}$. In the second case, the contact between some number of atoms at the osculating surfaces is disrupted. The mobility of the atoms in the free part of the surface is greater than in the contact sections of same. Hence, the disruption of contact will increase the mobility of the disconnected atoms, and contact between them will be renewed, while mobility will again diminish. This results in a dynamic equilibrium -- the disruption of the contact induces an increase in the mobility of the atoms; the increase in the mobility of the atoms leads to a "healing-up" of the initial contact; the "healing-up" of the contact, in turn, is manifested in the reduction of the mobility of the atoms to its initial value, and so on. During this process, the mobility of the surface atoms themselves is [further] increased. This increase is in direct ratio

to the number of atoms, the contact between which is disrupted in a unit of time, i.e., again in direct ratio to the rate of creep $\dot{V}$. In both the first and the second cases, there is a direct ratio between the number of atoms, reciprocally exchanging mobility in a unit of time, and the rate of creep.

Let a constant rate of creep $\dot{V}$ be established in the presence of some external stress σ . With an increase in stress by $d\sigma$, the increment in the rate of creep $d\dot{V}$ equals the increment in the number of atoms changing mobility in a unit of time. And this latter increment is to be at the same time directly proportional to both $d\sigma$ (compare with formula (59/4)), as well as to the entire number of atoms changing mobility in a unit of time, i.e., to the rate of creep $\dot{V}$. Hence,

$$d\dot{V} = k\dot{V}d\sigma \quad (59/6)$$

where k = constant.

By integrating, we derive the Ludwik rule:

$$\dot{V} = e^{k\sigma} + \dot{V}_0 \quad (59/7)$$

where e is the base of natural logarithms;

$\dot{V}_0$ is the mobility of atoms at zero load, or

$$\sigma = \ln \dot{V} - \ln \dot{V}_0 \quad (59/8)$$

The Ludwik rule is effective at very low rates of creep, about 10^{-8} to 10^{-5} percent per hour. When rates of creep become higher, it becomes necessary to take into account the effect of toughening. The factor of toughening retards the rate of creep

when the value of σ grows higher, and it can be calculated by dividing the right-hand part of formula (59/6) by σ .

Then

$$dV = nV \frac{d\sigma}{\sigma}, \quad (59/9)$$

where $n = \text{constant}$

By integrating formula (59/9), we obtain:

$$V = k\sigma^n, \quad (59/10)$$

where $k = \text{constant}$.

At very low rates of creep, on the contrary, it is necessary to take into account recrystallization, and formula (59/6) may need corrections of another type. One such correction is the Kanter formula⁽¹¹²⁾:

$$d\left(\frac{V}{\sigma}\right) = k \frac{V}{\sigma} d\sigma, \quad (59/11)$$

whence

$$\frac{V}{\sigma} = e^{k\sigma} + \left(\frac{V}{\sigma_0}\right), \quad (59/12)$$

where $k = \text{constant}$; $\left(\frac{V}{\sigma_0}\right)$ is fluidity at zero load.

Finally, at the very lowest rates of creep, deformation may take place entirely at the expense of only the atoms at the grain boundaries, without drawing into circulation the internal atoms, and without increasing, in the process, of the mobility of the grain boundary atoms themselves. In such a case, the metal will sustain deformation in a manner similar to that of a homogeneous amorphous substance, and the rate of creep under load will

vary as per formulas (59/3) and (59/4). Deformation of such a type is possible only in the presence of a very low rate of creep, which does not perceptibly increase the process of mobility exchange between the atoms.

Formulas (59/6) and (59/12) have one thing in common, and that is the variable nature of fluidity $\frac{V}{\sigma}$ (and the inverse to the latter magnitude of viscosity $\frac{\sigma}{V}$). Fluidity increases greatly with increase in load.

Footnote. The increase of fluidity with higher loads may also be explained by the increase in the number of higher-mobility surface atoms, as a result of the distorting effect of the load upon the surface of the grain.

From formula (59/7):

$$\frac{V}{\sigma} = \frac{e k v}{\sigma} + \frac{V_0}{\sigma}. \quad (59/13)$$

From formula (59/10):

$$\frac{V}{\sigma} = k \sigma^{n-1} \quad (59/14)$$

From formula (59/12):

$$\frac{V}{\sigma} = \frac{e k \sigma}{\sigma} + \left(\frac{V}{\sigma_0} \right). \quad (59/15)$$

Table 46 below is a compilation of data by Clark and White⁽⁸⁵⁾ relating to creep in brasses at various temperatures, rates, and loads. The values of exponent n in formula (59/10) $V = K \sigma^n$, computed by the author, are given in the last column of the table. The values of n were oscillating from 11 to 2, decreasing with the rise in temperature. With the rise in temperature, the differ-

ence in the mobility between the internal and surface atoms is diminished (see Paragraph 54). Therefore, the deformation of the metal approaches the deformation of an amorphous substance, and exponent n in formula (59/10) is decreased, converging in its limit value near the melting point, to one. In this limit case, formula (59/10) is transformed into formula (59/3), which is the formula for the deformation of amorphous substances and viscous liquids.

By the data contained in Table 46, the intensity of the growth in the mobility exchange between the atoms with temperature can be computed. For 77-22-1 brass at 315° Centigrade, $\sigma = 0.84$ kilograms per square millimeter, $\dot{\epsilon} = 10^{-5}$ percent per hour. At 200° Centigrade and the same load, the rate of creep, extrapolated by means of formula $\dot{\epsilon} = K\sigma^n$, is lower by billions of times. Hence, a temperature drop by 110° Centigrade induces a very intensive drop in the mobility of and in the mobility exchange between the atoms of the metal.

[see next page for Table 46]

TABLE 46

(85)
Creep in Brasses as per Clark and White

Grade of brass	Temperature of setting in of recrystalliza- tion in °C	Temperature of creep in °C	Proportional limit in rapid tension in kg/sq mm	Tensile stresses in kg/sq mm at rate of creep			Exponent in formula (59/10)
				10 ⁻⁵ % per hour	10 ⁻⁴ % per hour	10 ⁻³ % per hour	
[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]
70-30	>205, <260	205	9.1	8.9	13.6	20.0	6.6 - 5.7
		315	4.7	0.20	0.60	1.51	2.1 - 2.5
		425	2.8	-very small-			
70-29-1	>205, <260	205	14.7	9.1	13.3	20.0	6.1 - 6.5
		315	10.5	0.70	1.37	2.66	3.4
		425	5.6	0.038	0.102	0.35	2.1 - 2.0
85-15	>260, <305	205	4.9	6.2	8.4	11.9	7.4 - 6.6
		315	3.9	0.70	1.82	4.76	2.4

-319a-

-961-

[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]
60-40	>150, <205	150 205	5.2 3.5	6.3 1.40	8.4 3.33	11.9 8.05	8.0 - 6.6 2.7 - 2.6
77-22-1	>260, <315	205 315	5.6 2.8	7.35 0.84	9.10 1.75	11.55 3.71	1.09 - 9.6 3.2 - 3.1
59-40-1	>150, <205	150 205	9.8 4.2	8.40 2.45	10.50 3.99	17.05 6.58	10.3 - 6.4 4.7 - 4.6

CHAPTER IX

BAKING60. Definition of the Term "Baking"

The following basic processes take place during the baking of compressed and non-compressed powders:

Footnote. In this paragraph, for the time being, we are not concerned with the reduction of oxides in the process of baking, which is, as are the other processes, tied in with qualitative and quantitative changes in the contact surface.

(1). An increase in the mobility of atoms due to the rise in temperature.

(2). A change in the contact surface of the particles. The contact surface is usually increased in baking. Even in the case when, with the growth of the grain, the absolute value of the contact surface is decreased, its fraction, taken up by the sections of contact with relation to the entire surface, is, in the majority of cases, increased.

(3). The absorption of residual stresses localized in the places of contact. As a result of baking, the contact surface is transformed from a stressed into a non-stressed surface.

(4). Recrystallization. The growth of the grain takes place through the contact sections and, in this manner, constitutes one of the manifestations of the process of change in the contact surface.

(5). A change in the mechanical properties induced by the change in the size and the nature of the contact between the particles (the change in the contact surface and the absorption of residual stresses).

(6). A change in the entire surface of the particles, which change is also linked to the magnitude of the contact surface, since the growth of the contact sections is an unavoidable result of the migration of the atoms both from the other sections of the surface as well as from the interior of the particles.

(7). A displacement of particles -- volumetric changes in powders also depend on the magnitude and the nature of the contact. There can be no displacement of particles without a change in the contact surface, and vice versa.

Thus, all phenomena observed in the baking of powders, are directly or indirectly tied in with the quantitative and qualitative changes in the contact between the particles. It, however, becomes rational to set down the following definition for the term "baking": baking is a quantitative and qualitative change in the contact between the particles (bodies), produced by the thermal mobility of the atoms.

Footnote. In some special cases, it is more rational to contemplate baking as a change in the entire surface of the particle (body).

Jones advanced the following definition: "the term baking is used to convey the idea of what occurs when metal powders conglomerate under the effect of their surface forces of cohesion, and it

must be understood that, practically speaking, this operation is accompanied by the application of pressure and high temperature".(27)

Practically all foreign specialists, such as Wulff⁽¹⁵⁵⁾, Baetz⁽¹²⁾, Kieffer and Hotop⁽¹¹⁵⁾, and others, subscribed to this definition.

Nevertheless, the author considers this definition irrational, for the following reasons:

(1). In essence, the above is a definition of the term "cohesion" and not of the term "baking".

(2). In the above definition, the concept "cohesion", as produced by deformation under the effect of external forces (compression), and the concept "cohesion" as stipulated by the inherent mobility of atoms, are confused. Whereas, the difference between a self-contained motion and a motion produced by external forces, should be clearly reflected in scientific terminology. The subsequent ignoring of the differences between self-contained and induced motions will inevitably result in great inconveniences, such as the inability to define the difference between animals and plants, between live and dead organisms, and the like.

Table 47 below cites a number of differences between the processes of pressing and baking. It brings out the point as to how diametrically opposite the nature of these processes is, and as to how absurd it is to unify the concept "cohesion" in pressing and in baking into the one term "baking".

TABLE 47

Basic Differences between the Processes of Cold-Pressing and BakingCold-pressing

In pressing, the work of deformation and the formation of a contact surface between the particles is performed by external forces against the inherent forces of cohesion

Pressing is accompanied by a consumption of energy.

In pressing, internal stresses are formed. The contact surface, obtained in pressing is "stressed". Pressing is linked to the toughening of the metal.

Baking

In baking, the work of deformation and the formation of a contact surface is performed by the inherent forces of cohesion and is linked to the self-contained motion of the atoms (molecules).

In baking, there takes place a liberation of energy.

In baking, the residual internal stresses are absorbed. The contact sections, formed in pressing, are transformed from stressed into non-stressed. The formation of new contact sections is not linked to the evolution of stresses. In baking, the metal is de-toughened.

Cold-pressing

In pressing, any change in the volume of the structural elements can occur in the direction of diminution only.

In pressing, the change in volume occurs, first of all, at the expense of the largest pores.

The diminution in porosity, both interparticle as well as intraparticle, occurs primarily at the expense of a reduction in the volume, and not in the number of the pores. With the increase in density, the mean volume of the pores is diminished.

Baking

In baking, in a number of cases, there is a growth of the structural elements.

In baking, the diminution of the volume occurs, first of all, at the expense of the minutest pores.

With the diminution in the volume of the metal in baking, alongside of the disappearance and diminution in the size of some pores, there may occur a considerable increase in the size of other pores. With the increase in density, the mean volume of the pores is frequently increased.

Most of the pores are open and interparticle pores.

Density is distributed in a very non-uniform manner in different places in the briquette.

Powder briquettes, as well as non-compacted powders, are conglomerates of particles. The particles in the briquette retain, to a considerable extent, their individual apartness.

Cohesion between the structural elements of powder briquettes is weak. The plasticity of powder briquettes is negligible. Interparticle strength is small. Hence, the strength

Baking is frequently linked to the formation of closed and intraparticle pores.

In baking, there is a leveling off and a more uniform distribution of density.

In baking, the powdered metal is transformed from a conglomerate of particles into a conglomerate of crystallites, which have very insignificant individual apartness.

In baking, cohesion and plasticity are greatly increased. Interparticle strength grows considerably. Strength and other properties are determinable by intracrystalline

and other properties are determinable by inter-particle factors, and fracturing is of an inter-particle nature. Strength is, to a considerable extent, determined by the engagement of the particles. properties, and fracturing may be transcrystal-line. Strength is, to a considerable extent, determined by the cohesion of the grains.

The differences between a briquette and a non-compressed powder are of a quantitative nature only.

The displacement of substance under compression occurs principally at the expense of the displacement of particles, as per diagram in Figure 29.

Baked articles differ from compressed and non-compressed powders not only quantitatively, but also qualitatively.

The displacement of substance in baking occurs principally at the expense of the displacement of atoms, both within the particles, as well as from one particle into another.

61. Processes Occurring in Baking. Growth and Diminution of the Contact Surface. The Drawing Together and the Drawing off of Particles

In baking, one group of processes promotes the growth of the particles, while another group of processes, on the contrary, is instrumental in the diminution of the contact sections.

The basic process leading to the growth in the size of the contact surface in baking is the migration of the atoms to the contact sections, induced by the differences in the mobility of the atoms. This process is accompanied by the drawing together of the particles, shrinkage. (see Paragraph 62)

The opposite group of processes, which reduce the size of the contact surface is primarily comprised of the absorption of residual stresses, the now-regulated localization of shrinkage, and the individual changes in the particles (see Paragraphs 64 and 65). This group of processes leads to the drawing apart of the particles and the growth of dimensions in baking.

Finally, there are processes, which, depending on the conditions of their flow, are, in some cases, linked to the growth of the contact surface and the drawing together of the particles, while, in other cases, they are linked to the diminution of the contact surface and the drawing apart of the particles.

The end result of baking -- the growth or diminution of the contact surface, the drawing together or apart of the particles, depends on the group of processes that is predominant.

Each of the individual processes, conducive to the growth of the contact surface, is always linked to the drawing together of the particles. Inversely, each of the individual processes, conducive to the diminution of the contact surface, always leads to the drawing apart of the particles. However, the joint interaction of all the processes may result, in a number of cases, in such a phenomenon when, for instance, the drawing apart of the particles will nevertheless be accompanied by some increase in contact. Thus, in the baking of briquettes compressed from coarse powders, the contact surface between the particles may become increased, regardless of the growth of dimensions in baking.

The processes of deformation in powdered metal during the baking can be subdivided into several groups, and not by the result of their effect (the drawing together or apart of the particles). It is possible, for instance, to differentiate deformations, induced by stresses extending to a great number of particles, from deformations stipulated by the mobility of the atoms and localizing within the range of one or two particles. The displacements and the change in the form of the particles, evolved with the deformation of the first type, may be classified in the same manner as in compression, i.e., in accordance with the diagram in Figure 29. The displacements and the changes in the volume and the form of the particles, induced by the mobility of the atoms, do not fit into the diagram presented in Figure 29, and are to be segregated into a special type of deformation due to atomic mobility. This type of deformation, in its turn, can be subdivided into:

- (1). "Individual" or "internal" changes in particles, in which case the atoms change place within the limits of individual

particles (change in the form of the particles).

(2). "External" or "collective" changes in particles, in which case the atoms pass from some particles into the others (changes in the form and volume of the particles).

62. Growth of the Contact Surface and Shrinkage as a Result of

Atomic Mobility

It was shown in Paragraph 53 (Table 42) that the degree of mobility of the surface atoms depends on their location. The atoms in the inside of the contact sections possess minimum mobility. In the order of growing mobility, it then follows: the atoms at the boundaries of the contact sections, the atoms in the depressions and hollows of the surface, the atoms in the level sections, the atoms in the protuberances, promontories, and in the ribs of external angles, the atoms in the apexes of the external angles.

The mechanics of the growth of the contact surface and the drawing together of the particles in baking resolves itself to the same process of the migration of the atoms and changes in their mobility as occur in recrystallization. The difference between recrystallization and baking consists only in that, during the first phase of baking, at lower temperatures, the atoms are displaced principally within the individual particles, along their surfaces, while in recrystallization they are displaced from one grain into the other and athwart the contact sections. However, during regression (repose), which precedes recrystallization, the atoms are also displaced within the individual structural elements. Generally speaking, even in the very definitions of the terms "baking" and

"recrystallization" there is no difference in principle.

In its essence, recrystallization, as well as baking, resolves itself to the change in the contact surface between the structural elements of the metal.

The atoms in the contact sections are of a lesser mobility than in all the other sections of the surface. Therefore, a considerably greater number of atoms pass from the free (non-contact) sections than in the opposite direction. The atoms, newly entered into contact, lose a considerable part of their kinetic energy, as if transformed from a liquid into a solid state. The energy liberated in this process -- "the latent heat of diminution in mobility" -- is similar to the latent heat of solidification. A considerable part of the atoms, previously disposed in the internal layers, but now in the surface, as a result of the displacement of the surface atoms, the balance of that energy being consumed in raising the temperature of the metal.

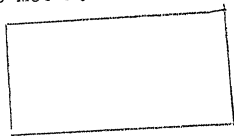


Figure 88. The diagram of shrinkage and growth in the contact surface: A. Particles prior to baking; B. particles after baking;
 1. layer of atoms which was disposed externally prior to baking;
 2. second layer of atoms (prior to baking).

Figure 88, is a diagram of shrinkage conducted in accordance with Wretblad and Wulff and somewhat modified by the author. The surface layer of the particles is filled in with a semiliquid or even an almost liquid mobile substance. This mobile substance, under the effect of surface tension, passes from the wide into the narrow pores in much the same manner as a blob of ink fills the capillaries

of blotting paper. The surface layers of two particles, in entering a pore, fill some of its volume, it being the case that the contact between them becomes enlarged, and the displaced semiliquid mass becomes solidified. With the displacement of the layer of the mobile substance, into the pores, a layer of immobile substance is denuded. The latter is transformed into a mobile state at the expense of a part of the energy, liberated during the increase in the contact surface, the "latent heat of diminution in mobility", and, in its turn, becomes displaced into the narrower pores, thereby bringing into contact new sections of the surface, etc. As a result of such constriction of substance to the places of contact, a shrinkage (i.e., a diminution in the volume taken up by the pores) and a growth of the contact surface take place. Thus, the contact sections act as a "pump", sucking in substance.

The phenomenon of shrinkage, i.e., constriction of metal to the places of contact, may be contemplated from two angles -- as induced by the difference in the mobility of the atoms in the free and the contact sections of the surface, and as stipulated by the effect of surface tension.

Some authors, as, for instance, Baets⁽¹²⁾, are inclined to ascribe the shrinkage in metal powders to surface tension. This opinion was advanced long ago for the explanation of shrinkage in non-metallic powders. Tertsagi and Gersevanov believe that shrinkage and the growth of strength in the kiln-drying of clay are due to the purely mechanical effect of the surface tension of water.

It must, however, be emphasized that surface tension can induce the displacement of the mobile atoms and molecules only.

The effect of surface tension is tied in closely with the mobility of a substance. Clay reacts with water, becoming thereby fluid and mobile. But if water is added to a gold powder or rosin, which substances do not react with it (i.e., the mobility of their atoms or molecules does not increase when water is added), the surface tension of the water will not induce shrinkage or the growth of the contact surface.

Price, Smithells, and Williams⁽¹²⁸⁾ were baking powders of tungsten with the addition, in one case, of copper, and, in the other case, of nickel and copper. In both cases, the baking took place at a temperature above the melting point of nickel and copper. No shrinkage occurred in the first case, since the copper, even though it wetted the tungsten, it did not react with it and did not accelerate the mobility of its surface layer of particles. In the second case, considerable shrinkage was observed as a result of the solubility of tungsten in the copper-nickel smelt and of the acceleration of mobility of the atoms in the surface layer of the tungsten particles. Hence, the deduction made by Price, Smithells, and Williams, that shrinkage cannot be explained by surface tension only, without taking into account of other factors, was perfectly correct.

In one of his articles⁽⁶⁴⁾, Frenkel' makes an attempt to explain the surface phenomena in baking by the effect of surface tension, while in another article⁽⁶⁵⁾, he explains it by the mobility of the atoms. He makes no final deductions as to which explanation is to be preferred.

It is the author's opinion that both these explanations do not exclude, but rather supplement one another. Indeed, any de-

formation is inevitably linked to a change in a stressed state, or vice versa. Hence, the displacement of the atoms, generally speaking, cannot be contemplated apart from the effect of forces. Such an isolated concept of the displacement of the atoms may be permissible in some particular cases for purposes of simplification only. In some cases it is convenient to explain shrinkage as due to the effect of surface tension. In other cases, on the contrary, it is convenient to proceed from the differences in the mobility of the atoms. However, the results flowing from both explanations must be the same, if no errors were admitted.

It must be remembered that the well known laws of equilibrium of forces are not always applicable to a powdered metal undergoing baking. Let, for instance, a powdered metal in baking be subject to the effect of compressive and tensile forces, the resultant of which, in accordance with the laws of mechanics, as applicable to an absolutely solid body, is equal to zero. However, in powdered metals, it is much easier to reduce than to increase the contact surface. Hence, the work and the effect of the tensile forces may be greater than the work and the effect of the compressive forces of the same magnitude, as a result of which the powdered metal will expand in baking. Hence, in many cases, the above explanations, when proceeding from the migration of atoms, carry with them a smaller risk of errors than they do when proceeding from the effect of forces.

Shrinkage takes place over relatively long periods of time. It is sometimes useful to contemplate deformation in shrinkage as creep induced by interatomic forces. The phenomena of creep are linked continuously to the inherent mobility of the atoms. Even

in the case of compact metals, due to the differences in the mobility of the atoms, creep cannot always be looked upon as the volumetric viscous flow of amorphous bodies (see Paragraph 59). Such a concept is even more inadmissible with relation to powdered metals, where the differences in the mobility of the atoms have an even wider range (see Paragraph 54). The error made by Frenkel' in one of his articles⁽⁶⁴⁾, where he conceives of creep in powdered metals as analagous to the viscous flow of amorphous bodies, is to be avoided. Such an analogy is admissible only in the case of baking coarse powders at high temperatures close to the melting point of the metal (see Paragraph 54).

Dynamically, the differences between the atoms in the free surface and the atoms in other areas of the crystal correspond to temperature differences lying approximately within the range of 25 to 70 percent from the melting point (see Paragraph 54). In the case of copper, it corresponds to a difference in the temperature of individual atoms of approximately 350 to 950° Centigrade. However, the total amount of excess kinetic energy is negligible. Even if the number of surface atoms attains 1 percent (see Paragraph 53, Table 43), upon the completion of shrinkage, when all the surface atoms pass into the contact sections, the liberated heat is capable of raising the temperature of the entire metal by 3 to 9° Centigrade.

It is possible that this evaluation is low and the kinetic energy differences between the atoms are equal to the difference between the corresponding energies of activation (see Paragraph 54). Thus, Frike, Lorman and Wulff discovered that the amount

of energy contained in a fine copper powder was greater than the same contained in a coarse powder by 3100 calories per gram-atom.

Alongside of the growth in the size of the contact surface, there is a diminution of the free surface of the particles. This diminution takes place not only as a result of the growth of the contact sections, but, to an even greater extent, as a result of the migration of the higher-mobility atoms from the promontories into the depressions, which is accompanied by the leveling off of the surface profile. As a result of these processes taking place in heating, the form of the particles undergoes changes. Desch⁽⁸⁹⁾, for instance, recorded the rounding off of angular particles in the heating of powdered gold. A thesis of exceptional interest was published recently by Lukirskiy⁽⁴¹⁾, to the effect that balls bored out from salt crystals, were transformed into polyhedrons by heating.. It may seem that the heating led to the increase in the number of the mobile atoms, since the surface of the polyhedron is greater than the surface of the ball. It must be remembered, however, that the number of maximum-mobility linear and angular atoms in such a polyhedron is less than in the ball, and that the total kinetic energy of the surface atoms has probably diminished in heating.

Footnote. It can also be deducted from the above that the higher-mobility atoms are not in an amorphous, but in a crystalline state.

At the beginning of baking, the temperature is below that for the setting in of crystallization (see Paragraph 57), since the atoms in the non-contact sections of the surface are of higher mobility than the atoms in the places of contact. Under the higher temperatures

of baking, the processes of shrinkage and recrystallization run their course simultaneously. The rate of shrinkage at high temperatures is approximately on the same order of magnitude as the rate of recrystallization. The extent of linear shrinkage may sometimes attain a value of 20 percent of the initial dimensions.

63. The Absorption of Residual Stresses

(7)

Already eleven years ago, the author of this book maintained that the absorption of the residual stresses of compression is one of the most important processes resulting in the diminution of the contact surface and in the increase in the dimensions of the powdered metal. External stresses in compression reduce the volume of the briquette, while internal stresses, on the contrary, tend to increase its dimensions. A partial absorption of the internal stresses takes place already at room temperature (the elastic after-effect, see Paragraph 36).

With the increase in the temperature and mobility of the atoms, the absorption of the residual stresses, which become localized in the places of contact, is increased. The non-reversible diminution of these stresses may proceed basically as follows:

(1). A diminution of residual stresses at the expense of the decrease or even a complete disruption of the contact sections.

(2). A diminution of residual stresses in the places of contact, on the contrary, as a result of an increase in the contact sections.

(3). A diminution of residual stresses at the expense of the

differences in the thermal expansion of the stressed and non-stressed sections, without being accompanied by any considerable change in the magnitude of the contact surface.

Footnote. In heating, there may also take place a reversible change in dimensions, if, during the rise and drop in temperature, a semblance of the previous disposition, as between the atoms of the distorted and non-distorted sections, is preserved. The modulus of elasticity is reduced in heating and increased in cooling. Hence, the residual stresses are diminished in heating and grow again in cooling. This is one of the causes of the adverse effect of internal stresses at low temperatures. It is probable that reversible diminution is of no particular importance in baking, since, with temperature, strength is diminished at a considerably more rapid rate than the moduli.

If the strength of the briquettes and the specific surface of the particles are low in magnitude, the absorption of the stress will follow the first course. But, in the presence of an adequate value for the strength of the briquettes and the specific surface of the particles, the process of constriction of the substance to the places of contact will rapidly raise the contact strength, diminish the contact stresses, and render the disruption of the contact impossible.

The energy consumed for the compression of a copper powder to full compactness, can raise the temperature of the entire metal 100° Centigrade. The work of compression goes not only into the formation of residual stresses in the places of contact, but also into the toughening of the metal particles to a rather considerable depth. The work involved in the absorption of the residual stresses

may be approximately evaluated on the basis of considerations submitted in Paragraph 43. In the case of copper, this energy, depending on the compression pressure and the percentage of residual stresses, corresponds to a change in the temperature of the entire metal from a fraction of a degree to 4 or 5° Centigrade. Thus, depending on the pressing conditions and the degree of dispersion of the powder, this energy, liberated during the absorption of the residual stresses, may be somewhat greater or less than the energy of shrinkage (see Paragraph 62). However, even in those cases when the work of absorption is greater than the energy of shrinkage, the processes of the drawing apart of the particles are by no means to be predominant (absorption may take place also in the presence of an increase in the surface of contact).

The differences in the energy charges, as between the individual atoms of a briquette, stipulated by the compression stresses, are of a smaller magnitude than the differences induced by their position in the crystals. The differential in the stressed state of individual spots in the briquette may be diminished with the degree of compressive reduction, and is, to a considerable extent, liquidated with the compressive reduction of the briquette to full compactness.

The residual stresses increase the mobility of the atoms in the contact sections of the surface, where their inherent mobility is lower than that of the atoms in the free sections of the surface. Thus, the stressed condition of the contact sections sort of smoothens out the differences between the mobility of the substance in the places of contact formed in compression and the mobility of the substance in the remaining sections of the surface. In the new

non-stressed contact sections, formed in baking, this difference is greater. Hence, the process of absorption may frequently develop by the way of substitution of the previous compression contact sections with new places of contact formed in baking. The presence of residual stresses, in some cases, may even promote the formation of new contacts at the expense of the greater tightening of the particles against each other.

It can be computed by formula $(43/2)$ that the linear expansion, in the presence of practically complete absorption of residual stresses, may attain a value of 5 to 10 percent. The total linear growth under the effect of the entire group of processes, which promote the drawing apart of the particles, rarely attains a value in excess of 5 to 6 percent. However, when fissures occur, its value may be as high as 15 percent.

64. The Non-Regulated Localization of Shrinkage

The phenomena of shrinkage have been treated in the literature of powder metallurgy, with the exception of the previous publications ^(2,7) by the author of this book, without relation to structural principles.

Whereas there are commonly known cases when the processes of shrinkage, i.e., the drawing together of particles, induce the formation of local disruptions and fissures, i.e., a local drawing apart of particles. For instance, in the desiccation of bread, cheese, clay, and like substances, shrinkage is frequently accompanied by fissuring. To prevent fissuring in clay, they frequently add sand, which, by diminishing shrinkage, also reduces the tendency to the

formation of fissures. Figure 89 shows typical fissuring occurring during the shrinkage of asphalt, argillaceous soil, plaster, and the like. The fissures subdivide the material into individual large regions (zones), which, in outline, resemble grains of cast metal. The formation of such isolated regions can only be explained by the fact that in each of them the direction of shrinkage of the particles (in the case of asphalt -- molecules) was orientated, as indicated by the arrows in Figure 89, toward the interior of the zone, as if its geometrical center. The fissures form at the boundaries of these regions of isolated shrinkage because of the movement of the boundary particles of the contiguous zones in opposite directions.

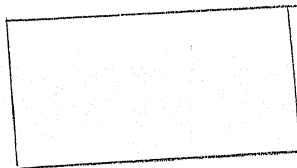


Figure 89. Diagram of zonal isolation

The author is consciously avoiding the use of the terms "center" and "nucleus", which are great favorites in metallography, and is substituting in their place the concept of region (zone) of isolated shrinkage. The terms "center" and "nucleus" are adequately precise for the description of crystallization of solidifying metal, when the number of grown grains equals the number of primary crystallization centers. But the use of these terms carries less precision when applied to the phenomena of recrystallization, and is entirely inapplicable to the process of shrinkage. The number of shrinkage centers is essentially equal to the number of contact points between all the particles, since shrinkage is localized about all the boun-

daries of the contact sections. The number of such "centers" for Figure 89 may run into billions, while there are only several regions of isolated shrinkage.

Let us analyze this in more detail. We shall begin with a most simple case, when the body undergoing baking, for instance, a cubelet, constitutes a sort of singular region of shrinkage. The deformations and stresses in the individual places of contact cannot be contemplated as being apart from the displacement and stresses in millions and billions of other contact sections. In a crowd, the movements and efforts of the individual are determined not as much by his free choice as by the general pressure and the direction in which the crowd moves. By the same token, in the baking of a powdered metal, the shrinkage and stress at each individual point depend on the general resultant forces and displacements relating to many billions of particles. Even in the presence of a single region of shrinkage and a perfectly homogeneous compression density, shrinkage cannot be uniform in all places (see Figure 90). If in each individual shrinkage nucleus, the stress and displacement shrinkages are directed toward the center, the pressure will be greater in the center of the cubelet than along its edges. Hence, the shrinkage will be at its maximum in the center of the cubelet, and its flat facets will become concave (see Figure 90,b).

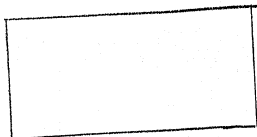


Figure 90. Shrinkage and growth: a. cubelet prior to baking; b. cubelet after shrinkage; c. cubelet after growth.

A reverse phenomenon is observed when the particles are drawn apart. The stresses, in this case, are directed from the center to the periphery, and, at the center, the maximum drawing apart of the particles occurs, and the flat facets of the cubelet become convex (see Figure 90,c).

Let us pass now to the various causes of formation of several or many regions of isolated shrinkage.

The causes of such isolation are frequently constituted by the internal stresses of compression. Let us imagine (as shown in Figure 91) that in a briquette, under the effect of internal stresses tending to elongate it in a vertical direction, hidden microscopic or even submicroscopic transverse lamellar fissures were evolved. These fissures divide the briquette into a series of transverse slightly curved layers. The internal stresses tend to break the bond between these layers. In turn, these stresses promote the same type of orientation for the shrinkage stresses in each isolated layer (Figure 91). As a result, the process of shrinkage still further isolates the individual layers, as can be seen in the fracture in the baked molding shown in Figure 37. Therefore, in a number of cases, the hidden exfoliation of the briquette, [which occurred under compression], comes to the surface and becomes visible during the process of baking (Figure 92). The separation of soap into shrinkage zones (Figure 93) is due to similar causes. The boundaries between the zones (fine fissures) are easily discernible, since the chemical reactions took place there.

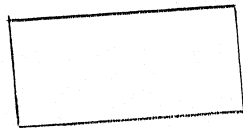


Figure 91. Zonal isolation of shrinkage stipulated by compression.

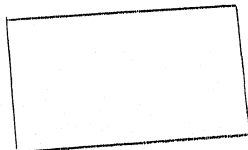


Figure 92. Hidden exfoliation -- the fissuring in a copper cubelet compressed from a powder with flat particles (copper ore concentrate slime) -- becoming visible after baking.

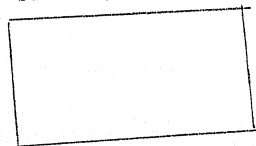


Figure 93. Insulation zones in the shrinkage of soap. X $1\frac{1}{2}$ times

In other cases, the briquette may be subdivided into conglomerates of particles. Each such conglomerate, in baking, usually constitutes an isolated shrinkage region, and it frequently occurs that, regardless of the considerable shrinkage inside the individual conglomerates, the shrinkage of the article as a whole is negligible (or even a growth in size takes place).

Isolation sometimes occurs as a result of non-uniform heating. Figure 94 shows a cubelet, in the center of which the temperature was lower than along the edges. As a result of the considerable shrinkage along the heated edges and the small shrinkage in the cold center, a defect was formed -- a so-called "core". It is impossible to eliminate this type of defect, since, when the tem-

perature is equalized, the already consolidated peripheral layer is not susceptible to deformation and thereby inhibits the shrinkage of the core.

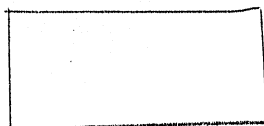


Figure 94. The formation of a core -- X 4 times

Finally, the process of isolation may develop as follows. In individual nuclei or groups of nuclei, the process of shrinkage may be more intensive than in other groups of nuclei (the presence of finer particles, local overheating, variations in density, and the like). The latent heat of atomic mobility will be liberated more intensively in these nuclei, as a result of which the neighboring particles will heat up to a point somewhat above the general level. This will lead to the intensification of shrinkage in the particles closest to the nucleus, and, consequently, to a further increase in the liberation of the latent heat of mobility, that will warm the subsequent layers of particles and, in its turn, increase their shrinkage. Thus, the isolated region, in which the shrinkage runs in a direction predominantly toward the nucleus, keeps on growing. The particles at the boundaries of two regions diverge in opposite directions, resulting in the formation of boundary voids.

The same process can be explained in a different manner. If a greater shrinkage occurred in some section, the latter will occupy a smaller volume. It being the case that the extreme particles of the section will pull along the particles of the next

layer, which, in turn, will pull along another layer, etc. If the extreme particles of the nucleus will not pull along the next layer of particles, a rarefaction will be formed around the nucleus. As will be seen from Paragraph 75, shrinkage in a powdered metal attains its maximum intensity in the places of lowest density. Hence, shrinkage is orientated toward such nuclei also in this case.

It should be noted that the microphotos show very rarely the presence of isolated regions. These become visible only in the case of the appearance of boundary fissures, or in the case when various chemical reactions have taken place in the above mentioned regions or at their boundaries. It should also be remembered that the zones of isolated shrinkage will not necessarily have a closed island-like outline. Their outline may also resemble that of a peninsula, in some place isolated from other regions, and in other places closely united with them.

It follows from the above that the drawing together of particles in some places is accompanied by the drawing apart of the latter in other places. Moreover, although at first it may seem completely incredible, the process of shrinkage, as a result of the formation of these isolated regions, may even lead to a total growth in the dimensions of the body as a whole. Let there be (Figure 95) in a metal three regions of shrinkage. There is an intensive shrinkage in the extreme regions A_1 and A_2 , while there is no shrinkage in the central region B. The directions of the resultant forces of shrinkage are indicated in Figure 95 by arrows. The shrinkage in the regions A_1 and A_2 can then

be conceived of as the creep in a porous metal under the effect of these (in this case, compressive) forces. But region B, as can be seen from Figure 95, is also under the effect of forces of the same magnitude as the regions A_1 and A_2 , with the only exception that the forces acting upon the porous metal are tensile. Hence, creep is also evolved in region B. The strength of porous metal in tension is always considerably lower than in compression. Therefore, the resulting magnitude of tension in region B may exceed the magnitude of compression in regions A_1 and A_2 , and there will be some total growth in the general volume of the metal.

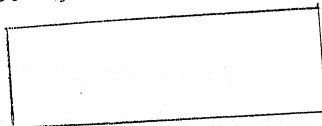


Figure 95. Diagram explaining growth in the presence of zonal isolation of shrinkage.

Let us note that in other fields of technology there are also cases of a diminution in density in the presence of non-homogeneous shrinkage. For instance, the non-homogeneous drawing together of atoms during the solidification of smelted metal leads to the obtaining of porous non-compact castings.

65. Individual Changes in the Particles

As already discussed in Paragraph 6, there takes place, in baking, alongside of the processes of the transfer of atoms from some particles into others (external or collective changes in particles), also the transfer of substance within the individual particles, which is linked to a change in their form, but not in their volume (internal or individual changes). For instance, the form of the

particles changes under the effect of surface tension, residual stresses, recrystallization of particle subdivisions, and the like. Such individual changes may be subdivided into changes localized at the places of contact (such as the constriction of atoms to the contact sections of the surface) and into changes non-regulatedly localized at other places.

The non-regulatedly localized individual changes in the particles are linked to the appearance of compressive forces and the consolidation of the powdered metal in some spots, and the evolution of tensile stresses and the de-consolidation of the powdered metal in other spots. It may seem at first that, since the total magnitude of the tensile and compressive stresses is the same, the total volumetric change in the powdered metal should equal zero. We have already indicated, however (in Paragraphs 62 and 64), that the laws of equilibrium of forces, effective in the mechanics of an absolutely solid body, cannot always be applied to a powdered metal. In a powdered metal, the drawing together of the particles (diminution of porosity) always requires a much greater force than the drawing apart of the particles (growth of porosity). Hence, an increase in porosity induced by a predetermined tensile force, is greater than a reduction in porosity under the effect of a compressive force of the same magnitude. In connection with this, the overall total of the effect of non-regulatedly localized individual changes in the particles will be an increase in porosity -- "individual isolation".

Figure 96 below is a rough diagram of the growth in porosity as a result of the individual isolation of the particles.

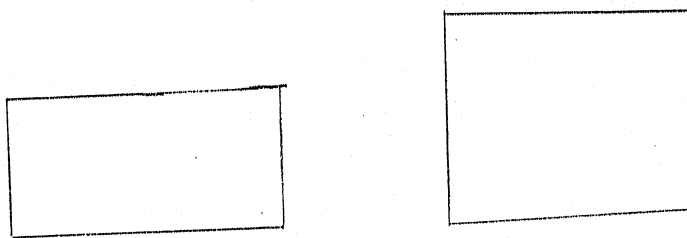


Figure 96. I. initial particles; II. the individual change in the particles.

Symbols

- particle boundaries;
- particle subdivision
- ▨ boundaries;
- pores

66. Thermal Expansion and Compression

As long ago as eleven years the author pointed to the importance of the reversible thermal expansion in the baking of powder metals⁽⁷⁾.

The thermal expansion of the particles in heating leads in a number of cases to the filling of the pores and to the growth in the contact surface. The contact newly established in compression frequently does not become discontinued in cooling. As a result, there is a non-reversible growth in the contact surface and a diminution in porosity. This process is of particular importance in the growth of the contact surface of medium and coarse particle powders (from several times ten microns and above).

In some other cases, thermal expansion is linked to the growth in porosity and the diminution in the magnitude of the contact surface (for instance, in the baking of briquettes consolidated to full compactness).

The process of cooling may induce an increase in porosity in the case of metals with isolated zones of shrinkage.

For the baking temperatures in practical use, the non-reversible linear shrinkage at the expense of the thermal expansion in heating cannot exceed 1 to 2 percent of the initial length, and the volumetric shrinkage, 4 to 6 percent of the initial volume of the briquette.

67. The Effect of Admixtures

The content of admixtures, particularly surface admixtures, in metal powders sometimes attains the value of 5 to 10 percent volumetrically. The principal admixtures are metal oxides, water, adsorbed and dissolved gases. Purely mechanical contaminations are less important.

Most of the admixtures are eliminated in baking. The evaporation of water sets in close to room temperature and is completed at 150 to 200° Centigrade (the boiling point for the water contained in the surface oxide capillaries attains the level of 200° Centigrade, and the elimination of chemically combined water sometimes requires even a higher temperature). The principal part of the adsorbed gases is volatilized at 100 to 200° Centigrade. The final elimination of the dissolved and chemically combined gases in vacuum heating occurs at considerably higher temperatures -- above the temperature of crystallization. Baking in a protective atmosphere (hydrogen, coal filling, etc.) may at times cause an increase in some admixtures. The oxygen is eliminated from the oxides during the reduction by the protective atmosphere, or during vacuum

baking, as a result of the dissociation of the oxide into the gas and the metal. The reduction temperature, depending on the type of metal and the physical characteristics of the powder, oscillates within the wide range from 25 percent to over 75 percent of the absolute melting point of the metal. Oxides of some metals, such as aluminum, generally, cannot be reduced by conventional baking.

The opinion, advanced by Trzebiatowsky⁽¹⁵¹⁾, that the growth of porosity in baking is due to the expansion effect of the liberated gases, is widespread in the literature on powder metallurgy.

The author, on the contrary, considers it necessary to emphasize that frequently (but not always) the admixtures of oxygen and water promote a diminution in the porosity and an increase in the contact during the baking process.

The negative effect of oxides and other admixtures principally consists in the diminution of the strength of the briquettes. This facilitates the breaking of the contact between the particles, thereby accelerating the effect of the processes which reduce the magnitude of the contact surface in baking. At times, however, the presence of oxides and moisture, on the contrary, will even increase the strength of the briquettes, as, for instance, in the case of the powders of tungsten and hard alloys. In these cases, the surface oxidation layer of the particles, reacting with the moisture of air, forms a sort of cement on the type of clay, which reinforces the briquette. This specifically is the reason for the practice,

which is sometimes resorted to abroad, of artificially humidifying the air in the press room up to a predetermined level. The opinion relating to the detrimental effect of the volatile gases is greatly exaggerated. The pores in powder briquettes are usually all of the open type, and the pressure of the gases is hardly in excess of 1 kilogram per square centimeter. By comparison with the tensile residual compression stresses, on the order of several thousand kilograms per square centimeter, the bulging out effect of the gases can be overlooked. Only in some special cases, when there is formation of a considerable number of closed pores at very high baking temperatures, the detrimental effect of the gases should be taken into account.

In many cases, the negative effect of oxides and moisture is more than compensated by their positive effect upon shrinkage and contact growth. It was mentioned in Paragraph 10 that oxidation increases the contact between the particles of the metal. When powders are stored in containers, which are not fully hermetically sealed, there sets in, at room temperature, the process of cohesion between the particles, which is due to the effect of moisture and air, and, after some time, the powder becomes a continuous lump. The term "cold baking", which Jones, without supporting reason, applies to the cohesion during cold-pressing, would be more in place, if applied to the process just described, which is similar to shrinkage in the desiccation of clay. In oxides, as in clay, water reacts with the surface layer of the particles, forming colloidal solutions, increasing the mobility of the surface layer, and subjecting the latter to deformation. With the evaporation of the water, there occurs a considerable transfer of substance from the non-contact sections, accompanied by shrinkage and growth of the contact

area. These mechanics of shrinkage are very similar to the effect of temperature upon the mobility of the atoms. Thus, these admixtures, in the presence of an adequate time lag at mere room temperature, promote an increase in contact area.

With the temperature rising, evaporation of the water and the above described process are accelerated. Grube and Schlecht⁽⁹⁴⁾ observed a high drop in the electrical resistance of nickel in a hydrogen atmosphere at the temperature of 80° Centigrade (see Table 51, Paragraph 70). Obviously, the diminution in resistance was induced by the growth of the contact between the particles. The drop in resistance was particularly great at 100° Centigrade (the boiling point of water under normal conditions) and somewhat above that. Tammann and Mansuri⁽¹⁴⁹⁾ observed the temperature at which the agitator stops during the heating and mixing of powders (Table 48 below). For all the metal powders in Table 48, as well as for a series of non-metal powders, the temperature of the agitator stop was about 130 to 150° Centigrade. Grube and Schlecht themselves consider this temperature as the one, at which crystallization sets in. However, Jones⁽²⁷⁾ maintains, and with good reason, that the temperature of the beginning of recrystallization can hardly fall within such a narrow temperature range for the above variety of metals (and non-metals). In the opinion of the author of this book, the only common property for all these substances is the boiling point of water in the capillaries of the oxidized surface layer (130 - 150° Centigrade).

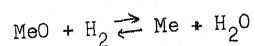
TABLE 48

The Temperature of the Agitator Stop for Powders with a Particle
Diameter of 0.3 - 1. Millimeter (as per Tammann and Mansuri)

<u>Metal</u>	<u>Melting point of metal at °C</u>	<u>Temperature of agitator stop in °C</u>
Tin	232	134 - 138
Cadmium	321	149 - 152
Lead	327	138 - 141
Zinc	419	141 - 150
Antimony	632	126 - 130
Silver	960	146 - 148
Copper	1084	144 - 148
Cobalt	1480	126 - 134
Iron	1530	144 - 155

The contact formed at such low temperatures under the effect of oxides and moisture, is not purely metallic, but is effected through a layer of admixtures.

With baking in a protective atmosphere under higher temperatures, the reduction of the oxides begins. For instance, metal oxides, in an atmosphere of hydrogen, are reduced as per the reaction below:



The rate of the reduction of the oxide powder is determined not as much by the rate of the above reaction itself, as by the time required for the diffusion of the hydrogen and the oxygen.

Hence, the rate of the reduction will increase greatly with the degree of dispersion and porosity of the substance, and with the temperature at which the reduction is accomplished. Thus, in accordance with Benton and White, highly dispersed copper oxides with a particle size of 0.1 micron were reduced in hydrogen of very high purity at the following rate:

at 170° C	in 1 hour
at 150° C	in 48 hours
at 130° C	in 9 days
at 115° C	in 10 days

Very fine nickel oxide powders were almost fully reduced, as per Stis' and Stevel', at 300°C within 15 hours.

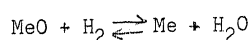
Under practical conditions, with a time lag of about 30 minutes, reduction probably exerts a perceptible effect, depending on the type of powder, already at baking temperatures on the order of 25 to 35 percent of the absolute melting point of the metal.

The elimination of the last remaining oxygen usually takes place at much higher temperatures -- on the order of 60 to 75 percent of the absolute melting point of the metal. The reduction of consolidated iron oxides Fe_3O_4 runs its complete course in a short time only at 1100° Centigrade (about 70 percent of the absolute melting point).

According to Leyter and Roberts, and also to Vant-Klev, the oxidation film on tungsten can be eliminated rapidly only at 2000° Centigrade (about 60 percent of the melting point).

The atoms in the ribs and angles [of the crystals] have higher inherent mobility (see Paragraph 54). The metal atoms in the oxides are disposed in an entirely different crystalline lattice than in the metal. Hence, the atoms of a metal just reduced are in a particularly non-stable state, have a minimum activation energy Q , close to zero, and have maximum mobility. These atoms will have a tendency for a transition into a state of minimum mobility, to the contact sections. The number of such atoms with activated mobility is considerably in excess of the number of all the surface atoms and attains the value of several percent of the total number of atoms.

The mobility of these atoms is activated only at the moment of reduction (in statu nascendi). However, the products of reduction (in the case of reduction in a hydrogen atmosphere, it is water) are not immediately eliminated from the baking atmosphere. The reaction of reduction



is reversible. In moisture-containing hydrogen there exist local supersaturations of water vapors, for which the reaction runs from right to left. This is particularly pronounced at the surface of the particles, since the metal is more permeable to hydrogen than it is to water. Therefore, the metal acts as a semipermeable partition, and, at the surface of the particles, the atmosphere is enriched by water vapors. With the thermal motion of the molecules of the water and the hydrogen, the supersaturation spots are constantly shifting. Therefore, the surface atoms are subjected continuously to intermittent oxidation and reduction, with repeat

activation of mobility at the moment of oxidation and at the moment of reduction, which process promotes the following:

(1). An increase in the rate of shrinkage and of the growth of contact at the predetermined baking temperature, or a reduction in the baking temperature required for the attainment of the predetermined rate of shrinkage and of contact growth at the expense of the activation of the mobility of the surface atoms.

(2). An increase in the contact surface at the expense of the increase in the volume of the material at the moment of oxidation; with reduction, the degree of contact attained is preserved.

(3). The successive oxidation and reduction increase the specific surface of the particles, contributing thereby to the increase in the rate of shrinkage (see Paragraph 73).

Thus, the presence of some oxygen or any other oxidation gas in the metal, in the protective atmosphere, or in specially introduced additions to the powder (ThO_2 , K_2O , Na_2O , KCl), activates the mobility of the atoms and the process of shrinkage in baking.

It is common knowledge that when reduction takes place in an atmosphere of moist hydrogen, the powder is baked more intensively than in dry hydrogen. Tammann observed that, in the process of annealing in thoroughly desiccated hydrogen, burnished nickel plate retained its luster up to a temperature of 400° Centigrade, while in hydrogen containing traces of oxygen the luster of the nickel plate was lost (as a result of activated atomic mobility) already at 300° Centigrade.

The recently published data by Jones and Hetzig⁽¹¹¹⁾ confirm the author's opinion that the negative effect of oxides, which are reducible in baking, results in the diminished strength of briquettes. With the oxidation of iron powders not prior to, but after pressing (about one hour after, by means of an air current at 400 to 500° Centigrade), the detrimental effect of oxidation upon the strength of the briquettes was eliminated. After baking the briquettes in an atmosphere of hydrogen, it was established that such preliminary oxidation imparted higher mechanical properties to the baked iron.

Non-reducible oxides, as in aluminum, exert a negative effect in baking. The mechanics of baking aluminum are still inadequately known. It is possible that, at high temperatures, the aluminum atoms at the boundary of the oxides are shifted, accumulating at the boundaries of the contact sections and reducing the surface of separation between the metal and the oxides. It is also possible that the surface oxides are gathered up from the films into a granular formation, that the continuous film covers are disrupted and forced off into other sections, and the like. The answer to all these questions is still in the future. However, as a result of research by Kremer and Cordiano, and others, the possibility of manufacturing metalloceramic products from aluminum powders has been established. The Kreislser Company in the United States has been manufacturing these for several years. Thus, non-reducible oxides, at any rate, are not insurmountable obstacles in baking.

68. Recrystallization

Shrinkage in baking is produced by the shifting of the

atoms along the surface, from the free areas to the contact areas.

With temperature, the mobility of the atoms is increased not only in the free sections, but also in the contact sections of the surface. The process of the growth of the particles in baking consists of the transfer of the atoms from some particles into others -- athwart the contact sections of the surface.

The atoms in the contact sections have lower mobility than the atoms in the free sections of the surface. Therefore, the growth of the grain must begin at somewhat higher temperatures than shrinkage. However, if, in shrinkage, during an infinitesimal moment of time, only the atoms near the perimeter of the contact sections take part, all the other atoms in the contact surface, too, will participate in the process of recrystallization. Hence, it may seem that the differences in the temperature, at which the above two processes set in, should not be particularly pronounced. In reality, these two temperatures are far apart. The causes of this phenomenon will be analyzed later.

In recrystallization, the shifting of the contact sections in a normal direction produces a reduction in the number of particles and in the absolute size of the contact sections. It being the case that a part of the structural element passes from a state of contact into a state of complete union, accompanied by the disappearance of boundaries.

In the presence of structural subdivisions within the particles, in addition to external recrystallization, i.e., the growth of the particles, there also occurs an internal (individual) recrystallization, i.e., the growth of the subdivisions of the

particles. Very frequently internal recrystallization sets in at lower temperatures, particularly when the structural subdivisions are submicroscopic in magnitude.

As a result of the growth of contact and of recrystallization in baking, the powdered metal is transformed from a conglomerate of particles into a conglomerate of crystallites (grains).

The process of recrystallization, directly in itself, does not produce a change in porosity. The atoms cannot jump across the pores, during the oscillations, athwart the surface. The filling of voids takes place not by the way of a frontal jump of the atoms across the pores, but by the way of a flank drawing up of the atoms from the free sections of the surface to the contact sections, or as a result of creep under the effect of internal stresses.

However, the indirect effect of the processes of recrystallization (both internal as well as external) upon the change in porosity during baking is very great (see Paragraph 71). Recrystallization intensifies the process of mobility exchange by the atoms and accelerates the rate of creep. Hanfstengel and Hanemann⁽⁹⁵⁾ established that, with the same temperature in tension, the rate of creep, in the presence of recrystallization, was 10 to 20 times greater than in non-recrystallized specimens. Hence, the temperature of the beginning of growth is linked to a considerable increase in the rate of the effect of processes which promote both the drawing together as well as the pulling apart of the particles.

Basically, the regularities in the recrystallization of powdered metals are reduced to the following.

(1). The growth of the particles of powdered metals sets in at much higher temperatures than the growth of the grains in compact metals. According to Sauerwald⁽¹³¹⁾, the temperature of the beginning of the growth of the particles of powdered metals is 66 to 75 percent of the absolute melting point of the metal. The recrystallization of compact metals, according to Bochvar, begins at temperatures on the order of 40 percent of the melting point of the metal.

(2). The internal recrystallization of the structural subdivisions of the particles (particularly the submicroscopic ones) frequently sets in at much lower temperatures than external recrystallization.

(3). The temperature of the beginning of growth of the particles is usually reduced with the increase in the degree of dispersion of the particles and with the presence in them of internal subdivisions.

(4). For most powders, the temperature of the beginning of growth of the particles and the ultimate size of the grain do not depend, as established by Sauerwald⁽¹³¹⁾, on the compression pressure.

(5). The presence of oxides in the initial powders and baking in a reducing atmosphere, with a small admixture of oxygen, reduce the temperature at which recrystallization sets in, and accelerate the growth of the grain.

(6). For fine powders, the temperature of the beginning of

external recrystallization is sometimes reduced with compression pressure. Also, the recrystallization temperature and size of grain are sometimes in strong relation to the treatment of the powder prior to compression.

(7). In the presence of deformation, the regularities of recrystallization in baked metals are the same as in cast metals.

The causes for the particular manner in which recrystallization manifests itself in powdered metals, were treated basically in the previous publications of the author^(2, 7). They are reduced to the following.

(1). The degree of individual apartness of the grains in compact metals approximates zero. In compact metals, the strength of the bond between the crystallites is great, and porosity is negligible. Hence, any individual change within a separate grain as, for instance, a change in form, may manifest itself only as a part of the general process of the external growth of some crystallites at the expense of others. In contradistinction, powders (both non-pressed as well as pressed) are conglomerates of individually isolated particles. In non-baked powdered metals the bond between the particles is so weak that, even with pores fully compressed, it is easily disrupted under the effect of internal stresses alone. In briquettes, the purely metallic contact, as shown by the study of its electrical conductivity (Paragraph 39, Table 35), is negligible (sometimes only a percentage of, or even a fraction of a percent of the total surface). Hence, dynamic change and approach to a state of equilibrium in the baking of powders, in contradistinction from the annealing of compact metals, may proceed not by one,

but by several courses, of which the basic ones follow below.

(a). The reciprocal translocation of particles.

(b). The individual (or internal) changes, occurring within the boundaries of individual particles and not connected with a change in their size (changes in form, the growth of the structural subdivisions). A change in the orientation of the boundaries between the particles may occur prior to the growth of the grain. In a recently published thesis by Harker and Parker⁽⁹⁹⁾ it is shown that the form of the particles, in the baking of powdered metal, approaches the most equiponderant, even in the absence of grain growth.

(c). The collective (external) changes, which do not fit within the boundaries of individual particles and which are linked to a change in their magnitude (the growth of the particles).

Thus, the growth of the particles is only one of several courses in the change of state of the system, and because of that alone, it may begin at higher temperatures than recrystallization in compact metals.

(2). Let us analyze the contact between a larger and a smaller grain in a compact metal (Paragraph 56, Figure 85). The total number of atoms in reciprocal contact, is exactly the same for each of the crystallites. However, the number of atoms of maximum mobility, in the angles and in the ribs, is greater in the contact section of the small grain. This specifically is the reason for the transfer of a greater number of atoms from the small into the large grain than the other way around. The situation is different for the same contact between a large and a small particle in non-baked powder (Figure 97). In this case, the contact is effected

over a very small fraction of the surface of each of the particles, and there is equality not only between the total number of atoms that are in reciprocal contact, but also in their distribution by the degree of mobility. Hence, although the transfer of atoms from one particle to the other may occur even at low temperatures, the difference as to the direction of the transfer will only become pronounced at such high temperatures, when shrinkage will preliminarily increase the area of contact to such an extent that the fraction of higher mobility atoms in the contact section will become smaller for the large particle than for the small one. Only then the growth of the grain begins. The growth of the grain without the preceding shrinkage would result in the increase of the surface of separation between the particles, without a corresponding reduction in the non-contact sections of the surface and in the amount of the free energy of the system. But this is hardly probable, since it is in contradiction to the second law of thermodynamics. Thus, the creation of a new adequately large contact surface is a necessary prerequisite for the growth of the particles.

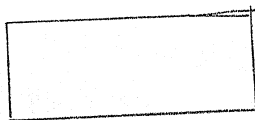


Figure 97. The diagram of contact between a large and a small particle in non-baked powders.

(3). The presence of a deep layer of surface oxides hinders the growth of the particles (a thin layer, on the contrary, may activate recrystallization). Therefore, the perceptible growth of

the grain will begin only at such temperatures when the rate of reduction, which is determined mainly by the time required for the diffusion of oxygen (see Paragraph 67), will approach the rate of mobility exchange between the atoms during recrystallization. At a temperature from 60 to 75 percent of the absolute melting point of the metal, complete reduction is usually accomplished in the practically standardized baking periods. For example, the temperature of 1000 to 1100° Centigrade is the temperature for the beginning of the growth of the particles for a series of iron powders, and is, at the same time, the temperature of complete reduction for consolidated iron oxides. The time for the diffusion of oxygen through the particles is reduced with the degree of dispersion of the latter and with the presence of intraparticle porosity. Simultaneously, there is a lowering in the temperatures for the reduction and for the beginning of recrystallization of the powdered metal. For instance, the temperature for the beginning of growth of the particles in high-dispersion carbonyl iron is about 700° Centigrade (see Figure 102), in lower-dispersion electrolytic iron, it is about 800 to 850° Centigrade, and for consolidated particles of iron reduced from slag, it is 1000 to 1100° Centigrade. Simultaneously, the temperature of 700° Centigrade is the temperature for the complete reduction of the oxidized particles of carbonyl iron, 800° Centigrade -- for the oxidized particles of electrolytic iron, and 1000 to 1100° Centigrade, for slag.

(4). The temperature for the beginning of recrystallization and the size of the grain, in most cases, have no relation to the compression pressure for the following reasons:

(a). The cold-pressing of powders, in contradistinction to the cold-working of compact metals, does not lead to any considerable reduction in size of the structural elements (see Paragraph 56).

(b). The cold-working of compact metals changes qualitatively the contact between the grains. The boundary contact surface becomes stressed in some places more, in some places less, while in other places it remains non-stressed. In powdered metal, the contact surface of the particles is continuously under the same critical stress. Hence, it is only the magnitude of the contact surface of the particles, but not its state, that changes with compression pressure.

(c). The initial contact surface in powdered metals, prior to baking, runs in direct ratio to pressure. However, the magnitude of the contact surface, attained by the powders, as a result of baking, at the moment of the beginning of growth of the particles, is comparatively little related to pressure (see Paragraph 75). In mildly compressed powders, the new contact surface grows rapidly, while in strongly compressed powders, on the contrary, the initial contact surface may even become diminished.

(d). The contact between the particles in pressing is effected through the oxidation film. In baking, the contact becomes metallic. The dynamic differences between toughened and non-toughened metal are completely negligible as compared to the dynamic differences between a metal and its oxide. This in itself is an adequate cause for the creation of a state, whereby toughening has no effect upon the process of external recrystallization in powdered metal.

(5). The lowering of the temperature of external recrystallization with the greater dispersion of the particles is due to the growth in the number of the maximum mobility surface atoms (see Paragraph 53), to the drop in the temperature at which the rate of reduction approaches the rate of translocation of the metal atoms, and to the slowing up of the elimination of the products of reduction through the minute pores.

(6). The drop in the temperature at which the growth of the particles and the increase in the size of the grain, in the presence of oxides in the powders or in the baking atmosphere, can be explained in the same manner as the mechanics of shrinkage and formation of a contact surface under the effect of these factors. The reaction of reduction $\text{MeO} + \text{H}_2 \rightleftharpoons \text{Me} + \text{H}_2\text{O}$ is reversible. Hence, while the reduction atmosphere contains the products of oxidation, the atoms of the surface layer of the particles are, alternately oxidized and reduced (see Paragraph 67). The increase in the mobility of the atoms is, in this case, equivalent to an increase in the baking temperature. In addition, the contact surface of the particles becomes greater (see Paragraph 67). All this stimulates the growth of the grain.

Footnote. Smithells preceded the author with the somewhat similar explanation for the growth of the particles in the reduction of tungsten oxides in moist hydrogen. The essential difference, however, was that Smithells maintained that the presence of water vapors promotes the evaporation of the tungsten oxides, which are precipitated from the gaseous atmosphere upon the largest particles. Thus, the explanation by Smithells is not general. He did not even extend

the particular case of his example to cover the growth of the grain in baking of tungsten, in the presence of oxidizing admixtures (ThO_2 , KCl , Na_2O). The first one to advance a generally applicable explanation of the causes for the growth of the grain, in the presence of oxygen, was the author of this book^(2,8,9).

(7). The drop in the temperature for the growth of the grain with compression pressure, in the case of very fine powders, can be explained in the following manner. In fine powders, it is not only the increase in the oxygen content, but, which is still more important, the considerable drop in gas permeability, due to which phenomena the products of oxidation are not eliminated through the pores for a long time. Hence, the growth of the grain is accelerated at low temperatures, and the temperature of visible recrystallization is reduced.

Let us assume that 5 percent of the atoms of the metal are oxidized, and following reduction, they will all become transferred from one particle into the other. This corresponds to a linear growth of the grain by 1.5 percent, i.e., for particles 1 micron in diameter by 0.015 of a micron. If the products of the reaction (H_2O or CO_2) should be eliminated immediately, recrystallization would stop, and could not even come to be noticed. Hence, further growth depends on how long the products of the reducing reaction remain in the pores of the metal. Permeability varies in direct ratio to the square of the diameter of the pores, i.e., in the absence of the association of the particles into conglomerate rates, in direct ratio to the square of the diameter of the particles (see Paragraph 12). It follows from this that in powders with particles of 1 micron size, permeability (i.e., the velocity of the circulation of gases

through the pores), in the absence of association into conglomerates, is 10,000 lower than in powders with 100-micron particles. Very fine particles are practically always associated into conglomerates, which are disrupted in compression. Hence, permeability drops considerably with compression pressure, by tens and hundreds of times (see Paragraph 40). Conformantly, the time of the presence of the chemically combined oxygen in the baking atmosphere is increased.

This explains the relation of the temperature of recrystallization to pressure, which relation Smithells, Pitkin, and Avery⁽¹⁴²⁾ discovered in the case of the highly dispersed powders of tungsten, and Dawid -- in the case of iron powder with 1-micron particles (see Table 49).

The effect of the repeat screening of tungsten for elimination of undersize, observed by Hüniger (104), can be explained in a similar manner (see Table 50). As a result of the repeat screening, prior to pressing, the size of grain in the baked tungsten moldings was increased many times (by 100 times in 20 screenings), as compared with the specimens prepared from the unscreened powder (baking conditions in all cases were the same).

Hüniger herself explained this effect by the considerable toughening of the tungsten in the screening. The incompetence of such an explanation is obvious. It is the opinion of the author that the above phenomenon is due to a drop in permeability and velocity of circulation of the gases through the tungsten briquettes as a result of the disruption of the associations of particles by the preliminary screening.

TABLE 49

The Growth of the Particles of Iron Powder, with Initial Particle
Size of 1 Micron, as a Result of 1-Hour Baking

Baking temper- ature in °C	0	230	4400	8800
200	Unchanged	Unchanged	Unchanged	Unchanged
400	"	Regression(1 μ)	Indications of regres- sion (1 μ)	Indications of regres- sion (1 μ)
600	"	"	Regression (1)	Regression (1 μ)
700	"	"	2 - 3 μ	2 - 8 μ
800	"	"	5 - 15 μ	3 - 7 μ
1000	5 - 10 μ	10 μ	15 - 60 μ	15 - 70 μ
1200	--	5 - 40 μ	15 - 80 μ	15 - 80 μ
1400	up to 250 μ	up to 250 μ	up to 250 μ	up to 250 μ

TABLE 50

Size of Grain in μ in Baked Tungsten Mouldings in Relation to
Preliminary Screening of the Powder (as per Hüniger)

Powder	Unscreened	Screened once	Screened 4 times	Screened 20 times
W + 0.75% ThO ₂	300 μ	400 μ	4000 μ	30000 μ
W + 1.5% ThO ₂	2000 μ	12000 μ	--	--

In baking, the amount of oxides and porosity are diminished, the contact between particles is increased, a stressed contact is transformed into a non-stressed one, the strength of the bond is increased. Hence, a metal that was baked after having sustained deformation does not, by the regularities of recrystallization, differ from a cast metal.

CHAPTER X

THE EFFECT OF BAKING CONDITIONS69. Evaluation of the Baking Process Cycle

The magnitude and the state of the contact surface of the powder particles undergo a change in the process of baking. Con-
formantly, all the other properties of the powdered metal, such as
structure, porosity, electrical conductivity, etc., also undergo a
change. A study of these properties makes it possible to arrive
at an approximate evaluation of the processes taking place in baking.

The electrical conductivity of the powdered metal grows in pro-
portion to some power to which the contact surface is raised. The
value of the exponent of this power, in the case of a purely me-
tallic contact, lies between 1 and 2. The transition of the con-
tact from a non-metallic to a purely metallic state also increases
electrical conductivity.

The ultimate strength and, particularly, the yield point in
tension vary approximately in proportion to the contact surface of
a single layer of particles. However, they run in relation not only
to the magnitude, but also to the state of the contact surface. In
baking, the contact gradually changes from a non-metallic to a
metallic state, from a non-stressed to a stressed condition, from
a state of engagement [between the particles] to a state of co-
hesion. All this increases the tensile strength.

The ultimate compressive strength of baked metals is usually
2 to 15 times greater than its ultimate tensile strength. This is

due to the fact that the contact surface in a porous metal becomes reduced in tension, while porosity is increased. The reverse is true in compression. With the progress of the baking process, the differences between the tensile and the compressive strength are usually somewhat reduced. Compressive strength grows with the size of the contact surface and also with a reduction in the amount of oxides. In some cases, it also grows somewhat with the diminution in the residual stresses, in connection with the accompanying increase of the ultimate degree of deformation. At times, on the contrary, it is decreased with the disappearance of residual stresses, as a result of easing deformation.

Hardness and the moduli of plastic deformation undergo changes with the progress of the baking process in a rather complex manner. The removal of the cold-hardening effect and the reduction in the amount of oxides during the baking process reduce the above mechanical properties, while the growth of the contact surface and density, on the contrary, promote an increase of the same.

Plasticity is greatly increased in baking. Tensile elongation in powdered briquettes equals zero, while after baking considerable tensile elongations are observed.

Changes in linear and volumetric dimensions, as indicators of the baking progress, are less sensitive than are electrical conductivity and strength. Let us remind our readers that in compression, the volume changes according to an arithmetical progression while the contact surface and strength change according to a geometrical progression. In baked metals, a reduction in porosity

by 1 percent usually corresponds to an increase in strength and in the contact surface by 3 to 10 percent. At low baking temperatures and low compression pressures, the reduction of porosity by 1 percent may be linked to an even greater increase in strength. Nevertheless, the evaluation of the baking progress by linear or volumetric shrinkage is a widespread practice, due to the simplicity and precision in their determination. Usually, the growth of density in baking is linked to an increase in all mechanical properties.

The magnitude and state of the contact surface and the combination of mechanical properties are characteristic of the bond between the structural elements of the powdered metal. This complex of properties is sometimes designated by the term "cohesion" (it is difficult to find a more precise definition). A concept of cohesion may be had frequently on the basis of such qualitative tests as the absence of crumbling particles when scratching the metal, the external appearance of a fracture, and the like.

The baking process is usually aimed at an increase in the cohesion of the powdered metal up to a predetermined limit (not always the maximum limit).

In baking, the properties of powdered metals change in relation to very many factors. In order to segregate the effect of one of these factors, the properties of the metal in relation to this factor alone, all other factors being equal, is analyzed. Thus, in analyzing the effect of the degree of dispersion of a powder upon the baking process, only dispersion is considered as the variable, while all the other factors, such as the composition of the metal, the temperature and the time of baking, the protective atmosphere,

and the like, are considered constants.

In so doing, certain difficulties appear, as to, specifically, which characteristic is to be selected as the measure of the same degree of consolidation of the powder. A comparison of powders compressed under the same pressure (isobars), as accepted by the majority of foreign specialists, is tied in with substantial inconveniences. The compression pressure is a "gross"-pressure (see Paragraph 18), made up of the pressure losses to friction plus the "net"-pressure, which alone effects the consolidation of the product. Figure 98 is a diagram depicting the results of the author's experiments with small copper cylinders of various heights, compressed from the same powder under the same pressure and baked under the same conditions. However, the net pressures were not the same, in connection with which the lowest briquettes had a porosity of 9 percent, and the tallest briquettes, a porosity of 23 percent. In baking, the tallest briquettes showed a volumetric shrinkage of 5.7 percent, while the lowest briquettes, on the contrary, showed a growth in volume of 5.9 percent. This example illustrates the inconvenience entailed in the use of the above mentioned isobars for the baking analysis. A precise determination of net pressures comes up against a series of practical difficulties. The experience of the author with specimens of various dimensions, compressed to the same degree of consolidation, have shown that, in this case, shrinkage does not depend on the dimensions and the shape of the products. In addition, the correlation between density (porosity) of the briquettes and shrinkage (see Paragraph 75), the contact surface, and other properties of baked products is usually

pronounced with more regularity than the correlationship between the above characteristics and compression pressure. Hence it is more convenient to analyze the effect of the various factors in baking not with the aid of the isobaric, but with the aid of the isopycnic diagram -- for specimens compressed to the same density.

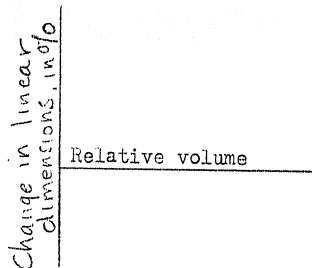


Figure 98. 1. Change in dimensions, after baking, in a longitudinal direction; 2. same in a transverse direction; 3. h_k of the briquettes (pressure of 5750 kilograms per square centimeter, baking for 1 hour at 800° Centigrade).

70. The Effect of the Baking Temperature upon Contact, Shrinkage, and Mechanical Properties

The effect of the baking temperature can be divided into several stages.

The first stage is characterized by the non-metallic contact between the particles. During this stage, the increase in contact, the growth of strength, and negligible shrinkage are due mainly to the evaporation of water from the surface layer of oxides. In this case, the shrinkage and the growth of contact are the same as in the desiccation of clay (see Paragraphs 12 and 67).

At this stage, shrinkage may occur also at the expense of the

thermal expansion of the particles. A shrinkage of this type, in the presence of a temperature raised by 100 degrees, may attain the value of 0.1 to 0.2 percent linearly, and 0.3 to 0.6 percent volumetrically.

Seemingly, the shrinkage and the growth of contact in heating, at this stage, would have been greater, if the elongating effect of the residual stresses of compression were absent. This is adequately confirmed by the experiments conducted by Kantorovich⁽¹¹³⁾ and by the author of this book.

When heating up to 80 - 100° Centigrade a tungsten powder that was compressed under a pressure of 4200 kilograms per square centimeter, after pressing and unloading, Kantorovich observed a high increase in electrical resistance. In the opinion of the author, this increase was due to the disruption of the contacts displaced during the thermal expansion of the particles, under the effect of the residual stresses. If the heating took place after pressing, but before unloading, the resistance, on the contrary, dropped considerably (more than by one third). Obviously, the contact increased in the heating as a result of thermal expansion and evaporation of water, could not, in this case, be disrupted by internal stresses, since they were hindered by the external load that was not removed.

The author of this book baked briquettes from iron powders mixed with soda at 1100° Centigrade. The internal tensile stresses were absorbed in the baking, but the presence of soda in the pores hindered the process of shrinkage. After the soda was washed out of the pores, a repeat baking at 150° Centigrade was conducted for

one hour, resulting in a shrinkage of about 2 or 3 percent volumetrically. Normally, the shrinkage of iron at 150° Centigrade does not exceed 0.2 to 0.3 percent. Thus, the elimination of the tensile effect of the residual stresses of compression led to a considerable rise in shrinkage at low baking temperatures.

Table 51, compiled in accordance with Grube and Schlect, depicts the change in the resistance of a nickel briquette with the change in the temperature of annealing. Up to 60° Centigrade, a considerable rise in electrical resistance was observed. Seemingly, prior to heating, the electrical resistance of the briquettes is stipulated to a certain extent by the contact through the water films surrounding the particles (electrolytic conductivity). At low heating temperatures, this resistance drops as a result of the evaporation of these films. At higher temperatures, in connection with the evaporation of water from the capillaries of the oxides, the growth of the non-metallic contact surface begins (as during the desiccation of clay). Therefore, resistance dropped perceptibly at 80° Centigrade, and at 100° Centigrade (the boiling point of water under normal conditions) the drop in resistance was particularly pronounced. At this temperature, approximately, the first stage of baking was completed.

In the first stage of baking, as was shown by the author⁽²⁾, the specific surface of the particles may become somewhat increased. Depending on the strength of the briquettes, either a small shrinkage (about 0.1 percent linearly), or a negligible growth on the same order of magnitude may be observed during the first stage. Sometimes, there is no change in dimensions registered.

TABLE 51

Resistance of Carbonyl Nickel, Compressed under a Pressure of 6000
Kilograms per Square Centimeter, when Heated or Cooled in Hydrogen
(as per Grube and Schlecht⁽⁹⁴⁾)

Tempera- ture in °C	Resistance, 10 ⁶ ohms		Tempera- ture in °C	Resistance, 10 ⁶ ohms	
	Heating	Cooling		Heating	Cooling
20	101.0	11.3	300	46.0	33.8
40	105.5	--	400	57.7	41.0
60	108.0	--	500	61.0	44.8
80	90.0	--	600	64.0	48.3
100	55.0	17.0	700	66.5	52.2
120	34.0	--	800	67.25	56.0
140	33.0	--	900	67.6	59.6
160	33.0	--	1000	68.0	63.4
180	33.2	--	1100	68.0	67.0
200	34.6	24.6	1140	68.0	68.0

The second stage of baking is characterized by the reduction of the oxides, i.e., by the qualitative change in the contact. This stage, within a certain temperature range, may run in conjunction with the first stage. It being the case that the contact is transformed from a non-metallic into a metallic contact, in connection with which the resistance of the metal, after cooling, drops considerably. While in a heated state, resistance becomes even somewhat greater, since the pure metal has a considerably higher thermal coefficient as compared to the oxides. This stage, like the preceding

one, is not accompanied by considerable shrinkage. The specific surface of the particles, too, is sometimes increased prior to the beginning of the third stage.

The third stage in baking is characterized by a considerable quantitative growth in the metallic contact at the expense of the mobility of the metal atoms, by the change in the shape of the particles, and by individual recrystallization. Almost in the entire temperature range, it runs jointly with the second stage (the reduction of oxides), the importance of which by now is, however, not so great. The third stage, depending on the degree of dispersion of the powder, begins at a temperature equal to 20 to 40 percent of the melting point of the metal involved. In the case of fine powders, this stage is characterized by a considerable rate of shrinkage, which cannot be explained by thermal expansion alone. In the case of coarse and highly compressed powders, on the contrary, there is the growth of the metal due to the absorption of residual stresses. The absorption of the residual stresses and the removal of the cold-hardening effect are probably complete by the beginning of the fourth stage of baking.

Most of the temperatures of the beginning of baking, as determined by various specialists, pertain to the beginning of the third stage. It is difficult, however, to specify with precision the temperature of the exact beginning of the baking of the metal proper, since both shrinkage and the growth of contact are observed already in the first and second stages. Hence, the determinations of adequately significant shrinkage and growth of contact are to a certain extent arbitrary. According to Smithells⁽¹⁴³⁾, the tem-

perature, at which perceptible shrinkage begins, is diminished with pressure, while, according to Grube and Schlecht⁽⁹⁴⁾, it does not depend on pressure.

In the third stage, there is a diminution in the specific surface of the particles, but no growth of the particles is observed.

The fourth stage is characterized by the complete disappearance of the oxides and the growth of the particles. Depending on the degree of dispersion of the powders, it begins at temperatures equal to about 50 to 75 percent of the absolute melting point of the metals involved and continues until the melting temperature is attained. During this stage, in connection with recrystallization, the rate of creep is greatly increased. Hence, the effect of the processes, promoting the drawing together as well as the drawing apart of particles, is increased. Figure 99, which is a shrinkage-temperature curve, depicts, at the temperature of the growth of the grain (800° Centigrade), a considerably reduction in volume for a copper powder of low and medium pouring weight, and, on the contrary, a considerable increase in volume for a coarser copper powder of a higher pouring weight. A very conspicuous process of zonal isolation in shrinkage and "individual isolation" -- non-regulatedly localized changes in the particles, are frequently characteristic for this stage of the baking process (see Paragraphs 64 and 65).

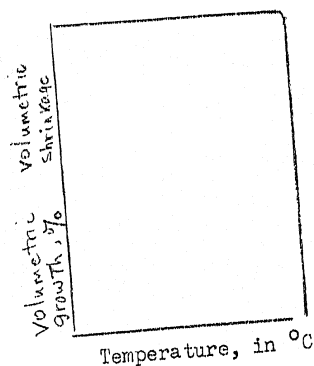


Figure 99. Shrinkage-temperature curve: 1. fine electrolytic copper, pouring weight 0.64 grams per cubic centimeter; 2. medium electrolytic copper, pouring weight 1.50 grams per cubic centimeter; 3. coarse electrolytic copper, 2.47 grams per cubic centimeter; 4. coarse, 3.51 grams per cubic centimeter.

The author baked coarse copper powder briquettes at 750° Centigrade for one hour, in which case the growth of the particles was observed. Upon cooling, the specimens were baked again at 850° Centigrade with the result that their volume was increased by 5 percent as compared with the results of the first baking. The residual stresses, probably, were fully absorbed in the first baking. The gases could not, in this case, have a bulging out effect, due to the absence of closed pores and to the considerable gas permeability of the specimens. Hence, the growth in the volume can only be ascribed to the processes of isolation of shrinkage and non-regularized localization of individual changes in the particles. In some cases (particularly in powders with considerable shrinkage), under very high temperatures, the local isolation of shrinkage is so considerable that, at first, there is (see Figure 99, the copper powder of low pouring weight) buckling, accompanied by a drop in density, then fissuring (overheating).

The clear subdivision of the process of baking into four stages is observed only in the case of fine powders. In the case of coarse powders, the stages are considerably concealed. Thus, the visible-shrinkage of coarse powders is frequently observed only when heated almost to the melting point of the metal.

The change in mechanical properties -- strength, hardness, ability to sustain deformation (deflection), and electrical conductivity, with the temperature of baking is depicted in the curve graphs shown in Figure 100. The changes in strength and electrical conductivity during the process of drinking run parallel with changes in density. They increase with higher baking temperatures, and decrease with lower ones. The indexes of the ability of baked metal to sustain deformation (elongation, deflection) usually become increased with higher temperatures, even though density and strength are decreased.

[See Figure 100 on next page]

Hardness and deformation moduli drop with temperature under the effect of detoughening and the reduction of oxides, and rise in connection with a diminution in porosity. Therefore, in specimens compressed to a high or medium degree, hardness first drops, then rises (detoughening is predominant), while in mildly compressed specimens -- it rises (increase in density is predominant).

The effect of temperature upon shrinkage can be explained as follows.

The processes of the drawing together and the drawing apart of the particles in baking can be conceived of as creep, induced

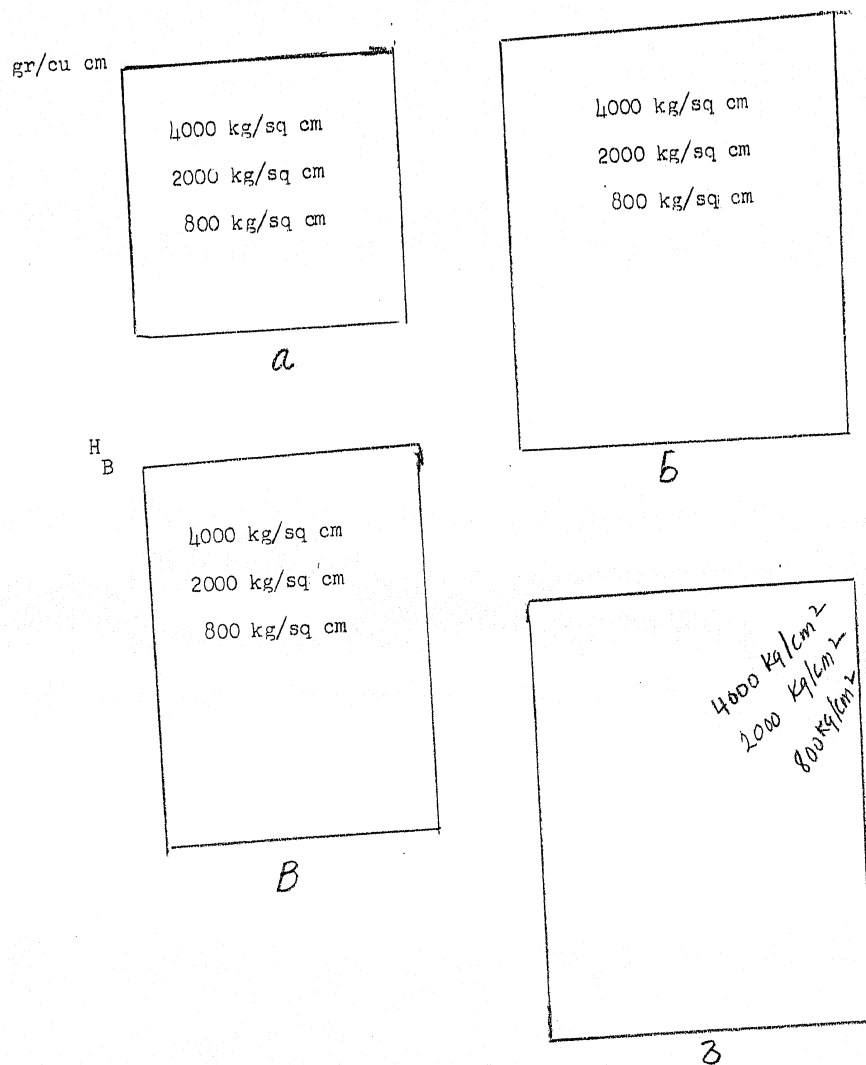


Figure 100. Curves depicting the mechanical properties of carbonyl nickel in relation to the temperature of baking: a. density; σ . ultimate tensile strength; B. Brinell hardness; Γ . electrical conductivity (as per Grube and Schlecht).

by internal forces. Table 52 shows that the capillary pressure, induced by surface tension σ , in the presence of a high degree of dispersion of the powder particles, may attain a value of several kilograms per square millimeter.

TABLE 52

Capillary Pressure for Particles of Various Diameters as Computed

by Formula $p = \frac{4\sigma}{d}$, with $\sigma = 1.25 \text{ gr/sq cm}$

<u>Diameter</u> <u>size d</u>	<u>Capillary</u> <u>pressure p</u>
1 cm	5 gr/sq cm
1 mm	50 gr/sq cm
100	500 gr/sq cm
10	5 kg/sq cm
1	50 kg/sq cm
0.1	5 kg/sq mm

In reality, the capillary pressure for particles of a given diameter should be greater than indicated in Table 52, since the actual specific surface of the particles is considerably greater than the apparent geometrical surface on account of the numerous roughnesses.

The rate of creep increases with temperature, stress, and the number of mobile surface atoms. In high-dispersion powders, capillary pressure is very great, therefore the rate of creep will attain conspicuous values, at which shrinkage will begin at a temperature equal to 20 to 30 percent of the melting point of the metal. However, in the process of creep, the surface of the par-

ticles will be diminished as a result of its smoothening. Alongside of this process, the capillary pressure and the number of mobile surface atoms will decrease. Therefore, the rate of creep at a given temperature will, after a certain time, drop to dimensions at which shrinkage will practically be discontinued. The higher the temperature, the greater the rate of creep, and the lower the value of the specific surface, at which shrinkage will be discontinued. Until the temperature of the external growth of the particles is attained, the magnitude of the surface may change at the expense of the smoothening of its profile. Therefore, shrinkage is small, since only several percent of the atoms lying near the surface take part in the translocation of the substance. With the attainment of the temperature of external recrystallization, with the smoothening of the profile of the surface, the effect of the forces, inducing a visible creep, is not yet exhausted. Therefore, the phenomenon of creep may continue even with the further diminution in the surface of the particles, at the expense of the grain growth. After a certain time the size of the grain will attain a certain value, at which the specific surface will so diminish that both the visible creep and the further growth of the grain will be discontinued. (Footnote. The time of the discontinuation of shrinkage and the time of the discontinuation of recrystallization must not necessarily coincide). Both shrinkage and the growth of the grain will be resumed again with a rise in temperature only. With the growth of the grain, the number of atoms drawn into the process of substance translocation is greatly increased, hence, the shrinkages, at the temperatures of external recrystallization, become greater. The above analyzed mechanism

of shrinkage and recrystallization at the expense of creep makes it possible to understand a series of details of these processes, such as the decrease in temperature at the beginning of visible shrinkage and recrystallization with the change in the degree of the dispersion of the powder, the reduction in the rate of shrinkage and grain growth with the time of baking, the independence of the setting in of recrystallization from compression pressure, etc. The rate of shrinkage at the prevailing baking temperatures attains the value of 0.1 and even 1 percent per minute.

The effect of the processes, counteracting the drawing together of the particles, also increases with temperature. Hence, a reduction in shrinkage may be observed with a rise in temperature.

The correlation between shrinkage and temperature may also be explained in a different manner. The process of shrinkage is the translocation of the fluid surface layer of the particles into the contact intervals and into the minute pores. The higher the temperature, the greater the fluidity, and the smaller the viscosity of the substance. Hence, with temperature, the constriction of the substance to the contact sections, and, consequently, the rate of shrinkage, is increased.

The quantitative ratio between the mobility of the atoms and temperature was discussed in Paragraph 51. The relative increase in atomic mobility with the rise in temperature is much greater at low than it is at high temperatures, while the absolute increase in mobility is always greater at high temperatures. In the presence of different temperatures, but with all

other conditions being the same (same initial powders and porosity of briquettes, same porosity of the metal at the moment of baking, for which the rate of shrinkage is computed), the rate of shrinkage is approximately in direct ratio to the mobility of the surface atoms which stipulate the shrinkage.

Most of the dilatometric examinations and measurements of electrical conductivity show that there is no visible shrinkage in cooling. The absence of visible shrinkage in cooling is due to two factors. On the one hand, at higher baking temperatures, the size of the specific surface of the particles may be so reduced that, when the temperature drops, the rate of creep becomes practically negligible. However, in those cases when the rate of heating is high, while the rate of cooling is low, a practically visible shrinkage in cooling may be observed. This occurred in one of the Hüttig experiments, when, during the cooling of a copper powder, a visible shrinkage was registered.

71. The Effect of Temperature upon Structural Changes -- the Link between Structural Changes and Shrinkage

Structural changes in relation to baking temperature are shown in Figure 101 (microphotos of electrolytic copper briquettes from the author's data) and in Figure 102 (microphotos of non-compressed carbonyl iron from the data by Schlecht, Schubard, and Duftschmid). The initial powders of carbonyl iron had spherical particles, subdivided into submicroscopic structural elements, 0.01 of a micron in size.

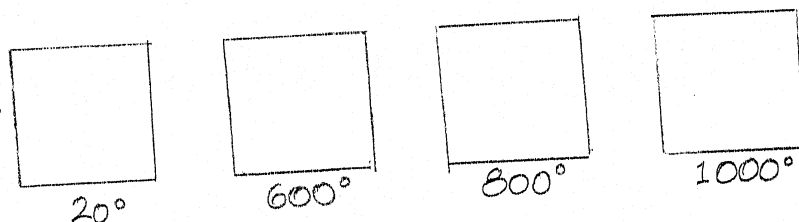


Figure 101. (Microphotos) [See text, page 247]

Change in structure during the baking of copper powders (initial porosity 40 percent) -- Pickled in HNO_3 -- X 500 times.

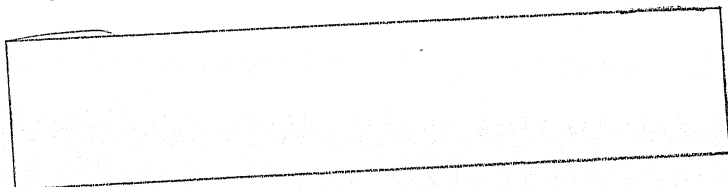


Figure 102. (Microphotos) [See text, page 248]

Change in structure and density during the baking of carbonyl iron powders (Schlecht, Schubard, and Duftschmid) X 1000 times.

In the case of carbonyl iron, the third stage of baking (see Paragraph 70) began at 400° Centigrade and ended approximately at 650° Centigrade. The following is characteristic of this stage.

(1). Individual (internal) recrystallization. At 400° Centigrade the particles departed from their original spherical shape, and the growth of crystallites within the individual particles began, practically ending at 650° Centigrade.

(2). A considerable smoothening of the profile of the particles is noticeable with the temperature rise from 400° Centigrade to 650° Centigrade. The specific surface of the particles, which was previously increased, is now reduced as a result of the smoothening of the profile.

(3). A visible reciprocal drawing together of the particles and a diminution of porosity.

(4). At the beginning of this stage, all the pores were open and intercommunicating. At the end of the stage, at 650° Centigrade, the isolation of the pores into individual more or less enclosed regions, and even the formation of individual more or less enclosed pores, is characteristic.

The beginning of the fourth stage (700° Centigrade) is characterized by the diminution of the specific surface of the particles due to external recrystallization (the growth of the particles). It being the case that the conglomerate of particles is transformed into a conglomerate of grains, which are completely dissimilar from the particles of the initial powders. Porosity is reduced considerably. At 700° Centigrade, the formation of intraparticle pores and the ever increasing isolation of the interparticle pores can be noticed. With the further rise in temperature, the formation of intra particle and closed pores keeps advancing. At 1200° Centigrade almost all the pores (both the intraparticle as well as the interparticle at the junctions of the grains) are closed ones. It is characteristic that, at 1200° Centigrade, the total porosity and the number of pores, as compared to the same at 800° Centigrade, has diminished, yet, the size of individual pores, on the contrary, has increased. The reduction in density at 910° Centigrade is due to the $\alpha - \delta$ transformation (see Paragraph 77).

The structure of the electrolytic copper powder changes in a similar manner. The fourth stage (the growth of the particles)

set in at 800° Centigrade. The microphotos in Figure 101 are very characteristic: alongside of the individual grains grown to giant proportions at 800° Centigrade, there are particles retaining the dendritic structure of the initial powder. At 1000° Centigrade, the predominance of intraparticle and isolated pores is characteristic. Figure 103 (a non-pickled microslide) shows clearly the isolatedness of the pores. The smoothening of the pore surfaces and their spheroidization, as a result of baking, are also visible.

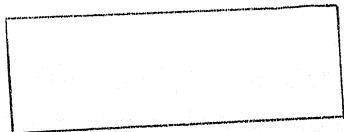


Figure 103. (Microphoto) [See text, page 249]

Copper powder baked at 1000° Centigrade, non-pickled, X 500 times.

In coarse powders, the structural changes are not as clear, and, at times, the particles and the pores between them retain their initial characteristics even at temperatures close to the melting point of the metal.

The fourth stage of baking is characterized not only by the growth of the grain, but also by the isolation of shrinkage. Figure 104 shows diagrammatically the link between the phenomena of shrinkage and the growth of the grain in baking. The formation of regions of isolated shrinkage is indicated by a directional arrow. In recrystallization, the region of isolated shrinkage may grow into one large grain with internal pores at the locations of the previous interparticle pores. As a result of such isolated shrinkage, the grown grains are separated from each other by voids, which hinder further recrystallization (Figure 104). With the

baking Temperature passing through a certain optimum level, the growth of the grain may be diminished in connection with the appearance of relatively small isolated shrinkage zones. Figure 105, which is a growth of the grain -- temperature curve graph plotted by Jeffries, indicates the presence of this optimum temperature (2600 - 2800 degrees centigrade), at which the size of the grain attains its maximum, in the case of tungsten powder with an admixture of thorium oxide. This isolation sometimes leads to a change in the macrostructure of the articles at high temperatures -- to buckling and fissuring (overheating). The effect of zonal isolation is particularly perceptible at high rates of shrinkage and recrystallization, i.e., in the baking of articles made from fine powders at high temperatures.

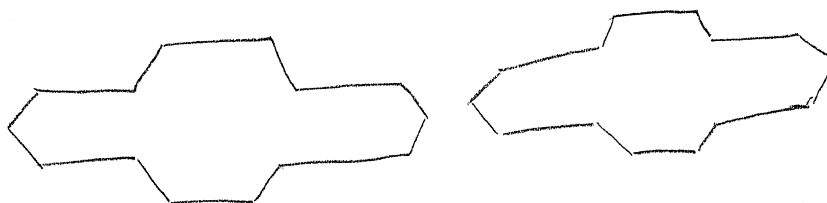


Figure 104. Diagram of the ratio between the isolation of shrinkage and the growth of the grain in baking (the pores are cross-hatched, the direction of shrinkage is indicated by arrows):

- a. the beginning; 6. the end of shrinkage and of grain growth.

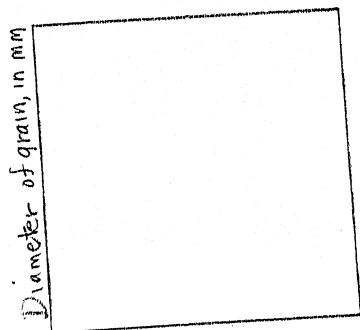


Figure 105. Ratio between the growth of the grain of tungsten powder and temperature (as per Jeffries).

Figures 106 and 107 show the changes in oil-absorbability, which factor is characteristic of the percentage of open pores and gas-permeability, determined by the size of individual pores -- in the case of coarse and fine copper powder briquettes at various baking temperatures.

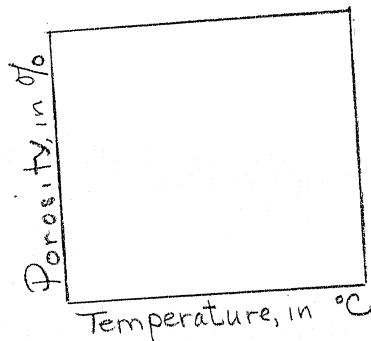


Figure 106. The change in porosity in the baking of copper briquettes: total porosity; the open pores fraction;
the closed pores fraction; I -- fine powders; II -- coarse powders.

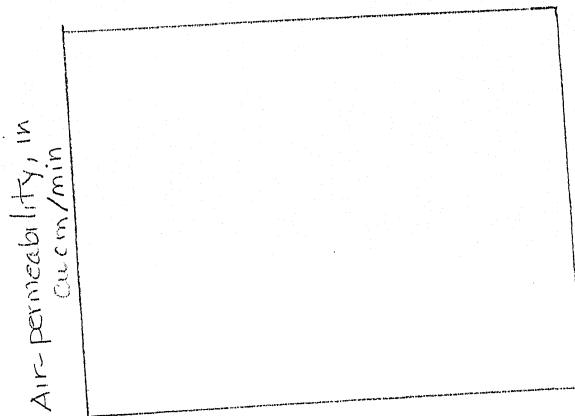


Figure 107. Change in air-permeability in the baking of copper briquettes: I -- fine powders; II -- coarse powders.

The following takes place.

(1). In the case of coarse powders, the percentage of open pores continuously remains the same (about 100 percent).

(2). The permeability of the specimens from coarse powders continuously grows with temperature.

This is due to the absence of the visible growth of the grain and of shrinkage at the investigated temperatures for articles made from coarse powders. Therefore, the disposition of the pores did not change and they remained open. Permeability rose with temperature as a result of the smoothening of the profile of the particles and the diminution of their specific surface which tied in with it. As a result, the streamlining of the particles was improved, and permeability enhanced.

In the case of fine powders, the following is character-

istic.

(1). The number of open pores is continuously diminished, while the number of closed pores is continuously increased.

(2). Notwithstanding the considerable drop in the number of the open pores, permeability grows almost continuously, diminishing only at 1000 degrees centigrade. Particularly characteristic is the rise in permeability with temperature, if it is considered in relation to the volume of the open pores.

In this case, both shrinkage and recrystallization, as already indicated above, are inevitably linked to the growth in the number of the closed pores. The smoothening of the profile of the particles reduces the friction of the gas current against the pore walls. The complete closing of the minutest pores reduces the ramification of the gas current and straightens its path. These factors and also an increase in the size of the individual open pores, in connection with the growth of the grain, may increase permeability with the rise in temperature to a certain predetermined limit. When this limit is exceeded, permeability is again diminished due to a pronounced drop in open porosity at the expense of shrinkage and of the closing of the pores.

The closed pores are frequently only difficultly-accessible, but not really "closed". Table 53 shows that different methods of impregnation result in the establishment of different percentages of closed pores.

TABLE 53

Percentage of Closed Pores in Relation to
the Method of Impregnation

<u>Method of impregnation</u>	<u>% of closed pores (in</u> <u>terms of total porosity</u>
Impregnation with spindle oil No. 3	
at room temperature, for 1 hour	31
Same as above, for 5 hours	28
Same as above, at 100° C, for 5	
hours	17
In vacuum	12
With viscous oil at room temperature,	
for 5 hours	36
With bakelite lac at room tempera-	
ture, for 5 hours	62

The number of difficultly-accessible pores is reduced in in vacuum, and also with a rise in the fluidity and a drop in the viscosity of the impregnation substance, with a rise in the temperature of impregnation (drop in viscosity) and the duration of the latter.

Shrinkage in baking may be compared with the impregnation

of the pores of a porous metalloceramic substance with a liquid. In this case, a substance of greater fluidity (in place of a liquid) is used to fill the pores from the surface of the particles. With temperature, there is a drop in viscosity, and a more complete filling of the pores is attained. It is also obvious that the gases will retard the complete filling of the pores, and that, in vacuum, a higher degree of shrinkage can be obtained. Hence, the passive effect of the gases upon shrinkage in baking, in all probability, is greater than their active bulging out effect.

The effect of structural changes in baking upon shrinkage is very great. The rate of recrystallization is determined by the product of the number of atoms participating in this process (the atoms in the contact surface) by some mean difference in their mobility. The rate of shrinkage is also determined by the product of the number of atoms participating in shrinkage, by the corresponding mean difference in mobility.

For the atoms, participating in recrystallization, the mean difference in mobility is many times below the mean difference in mobility for the atoms that take part in shrinkage, particularly at low temperatures (their approximate ratio is the ratio between the mean mobility of the active atoms in the contact sections of the surface and the mean mobility of the active atoms in the free sections of the surface). The number of the atoms participating in recrystallization, on the contrary, is, by many orders of magnitude, greater than the number of atoms participating in shrinkage (the ratio between these numbers is the ratio between the area of the contact sections to their

perimeter, i.e., in the case of circular areas, it is $\frac{n^2}{4}$ atoms: n atoms).

Hence, also the rate of recrystallization, particularly at high temperatures, may be greater than the rate of shrinkage.

In recrystallization, the contact surface, which acts as a pump transferring atoms from the distant sections of the free surface, is itself rapidly translocated toward them (see Figure 108,a). If, under these conditions, the rate of recrystallization is greater than the rate of shrinkage, the latter may become accelerated to attain the same order of magnitude as the former.

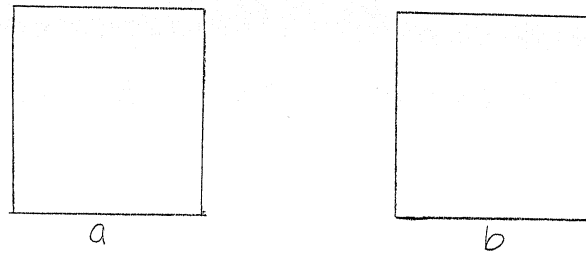


Figure 108. Diagram of the interaction between shrinkage and the growth of the grain:

a. the arrows indicate the translocation of the boundary (contact surface) of the grains in recrystallization and the counter-constriction of the atoms in shrinkage; b. the formation of an intracrystalline pore (the disappearance of the contact surface), linked to the discontinuation of shrinkage.

On the other hand, the same process of translocation of the contact pumps inevitably accelerates zonal isolation (see Figures 89, 104) and thereby reduces shrinkage, the contact surface, and the mechanical properties of the baked materials. In connection with the continuous base translocation of the shrinkage nuclei during recrystallization, with the discontinuation of shrinkage in some spots and its evolution in others, recrystallization may either accelerate zonal isolation, or induce it, if it was not already present prior to recrystallization. As a rule, the tendency to zonal isolation is increased with the rate of shrinkage and recrystallization (i.e., with the rise in the baking temperature and the degree of dispersion in the powder). Specifically, zonal isolation of shrinkage is the cause of the existence in a number of cases of an optimum baking temperature, which, when exceeded, results in a drop in density and other properties (overheating).

Recrystallization is linked to the transformation of the interparticle pores into intracrystalline pores (Figure 108, b). Shrinkage is stipulated by the presence of contact sections, acting as "pumps". These contact "pumps" do not exist in the intracrystalline sections. Therefore, the reduction in the volume of such pores is only possible at the expense of the volumetric viscous flow under the effect of surface tension. The rate of such volumetric flow (see Paragraph 54) is by several orders of magnitude lower than the rate of shrinkage in the presence of the translocation of the atoms from the free surface to

the contact surface. Hence, the closing of the intracrystalline pores cannot be completed within the practically-permissible baking periods. In addition, as noted by Frenkel' (64), the closing of such pores is retarded by the presence of the gases. The mechanical properties of baked metals, as a result of recrystallization, may, in a number of cases, become reduced in connection with the excessive growth of the grain.

72. The Effect of Baking Time

Figure 109 is a curve graph depicting two typical cases of the ratio between the volumetric shrinkage $\frac{\Delta V}{V_0}$ and the momentary rate of volumetric deformation $\frac{dV}{V_0 dz}$ (i.e., the relative change of the volume $\frac{dV}{V_0}$ during an infinitesimal time interval dz), on the one hand, and the time of baking, on the other hand. In one case, the total shrinkage is increased, at first rapidly, then at a slower rate. After some time has elapsed, the total shrinkage attains a constant value, which does not change any more with further baking time. In other words, the rate of shrinkage in this case is reduced to zero and remains at the zero level with a further time lag. In the second case, the total shrinkage after a certain time attains a maximum value and is then reduced with a further time lag. In this case, the rate of shrinkage does not stop at the zero level, but keeps on diminishing, having changed its algebraic sign. Hence, the powdered metal, in this case, having crossed the zero level of shrinkage, begins to expand at some rate.

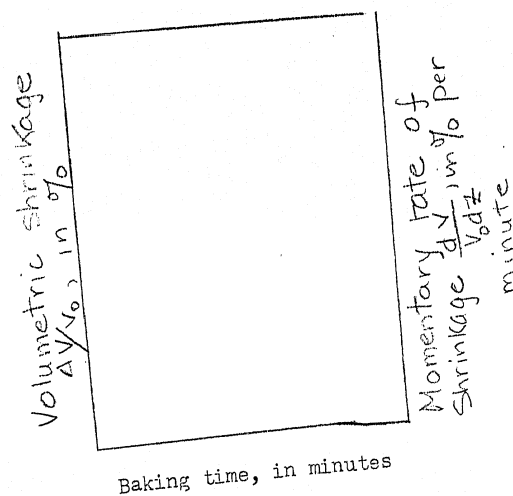


Figure 109. Ratio between volumetric shrinkage and momentary rate of volumetric shrinkage, on the one hand, and the baking time, on the other hand (at 700 degrees Centigrade), in the case of an electrolytic copper powder.

The rate of shrinkage can be conceived of as a result of creep under the effect of two groups of forces -- tensile and compressive.

Constriction of a powdered metal is caused primarily by the translocation of the mobile surface atoms from the free sections to the contact sections, and also by the filling of the pores during the thermal expansion of the particles. Constriction at the expense of thermal expansion will drop to zero very rapidly -- immediately upon the preliminary heating of the sample up to the time-lag temperature. The rate of constriction, due to the translocation of the higher-mobility

atoms, is determined by the product of the number of these atoms by their mobility. The diminution in the number of these atoms dn in an infinitesimal time interval dz equals:

$$dn = -kndz \quad (72/1)$$

where k is a coefficient proportional to the mobility of the atoms, constant at a given temperature, and growing with the rise in the latter. Integrating this equation, we derive:

$$n = e^{-kz}, \quad (72/2)$$

i.e., that the number of the higher-mobility atoms is rapidly diminished with temperature. Differentiating equation (72/2), we derive:

$$\frac{dn}{dz} = -ke^{-kz}, \quad (72/3)$$

i.e., that the rate of translocation of the mobile atoms $\frac{dn}{dz}$ is rapidly diminished with time to practically negligible dimensions.

If the effect of the processes, hindering the drawing together of the particles, is disregarded, the momentary rate of shrinkage $\frac{dv}{v_0 dz}$ and the momentary rate of consolidation $\frac{dn}{dz}$ within some interval, will be approximately proportional to $\frac{dn}{dz}$, i.e.,

$$\frac{dv}{v_0 dz} = ae^{-kz} \quad (72/4)$$

$$\frac{dV}{dz} = be^{-kz}, \quad (72/5)$$

$$\ln \frac{dV}{V_0 dz} = \ln a - kz, \quad (72/6)$$

$$\ln \frac{dV}{dz} = \ln b - kz, \quad (72/7)$$

where a and b are constants. Indeed, in some cases (Figure 110), such a ratio was observed between the momentary rate of shrinkage (consolidation) and the time-lag in baking.

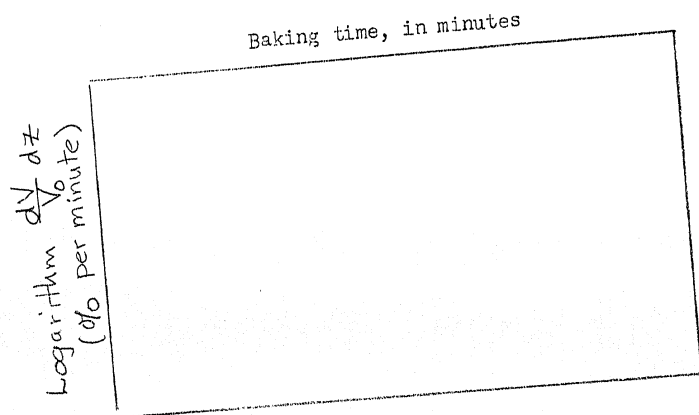


Figure 110. Ratio between the logarithm of the momentary rate of volumetric shrinkage $\frac{dV}{V_0 dz}$ of electrolytic copper and the time of baking (at 700 degrees centigrade).

If the processes of the drawing apart of the particles are disregarded, the ratio between the momentary ~~rates~~ rates of shrinkages (consolidation) of similar powders compressed to equal density at various temperatures, at the moments of time corresponding to the same density of the baked metal, will equal the ratio between the mobilities of the respective atoms at these

temperatures. On the basis of this assumption, the energies of activation of the atoms in the free surface of copper were established, as indicated in Paragraph 54.

In place of the ratio between the momentary rates of shrinkages, the ratio, which is equal to it, between the duration of the shrinkages to the same density at various temperatures, may be used.

Tension is induced by the absorption of the residual stresses of compression, by zonal and individual (see Paragraphs 64 and 65) isolation (zonal isolation is localized within the range of groups of particles, individual isolation, within individual particles). The rate of tension is also diminished with the time-lag, as a result of the diminution in the residual stresses and in the rate of the zonal isolation of shrinkage (which is reduced with the rate of shrinkage). The absorption of residual stresses is more rapid than the diminution in the rate of the zonal isolation of shrinkage. Some of the processes of the individual change in the particles, which produce tension, will, with the further time-lag, retain their rate at a certain low, but rather steady, level. For instance, localized oxidations and reductions of particles do not substantially change with the time-lag.

When the rate of compression is equalized with the rate of tension, the resulting rate of shrinkage drops to zero. If, with a further time-lag, the rates of tension and compression

are equally diminished, the rate of shrinkage remains at the zero level. If the rate of compression diminishes more rapidly than the rate of tension, the rate of shrinkage, with the time-lag, becomes negative, and porosity begins to grow.

In the baking of powders containing difficultly-reducible oxides on the surface of the particles, visible shrinkage may begin only after they have been reduced or otherwise eliminated. Hence, as shown in Figure 111, according to Wulff, in such cases, the rate of shrinkage will grow, and not diminish, with the time-lag.

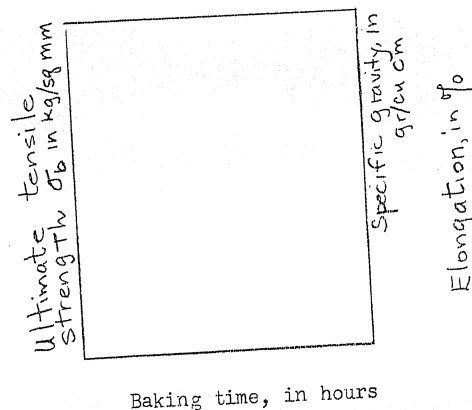


Figure 111. Ratio between density γ , tensile strength σ_b , and elongation δ , on the one hand, and the time-lag in baking, on the other hand -- in the case of 18 - 8 stainless steel baked at 1250 degrees centigrade (according to Wulff).

Figure 112 is a relative density-baking time curve graph showing the ratio between shrinkage and the duration of the time-lag for a medium and a high baking temperature. At high temperatures, shrinkage rapidly attains its maximum values, at lower temperatures, the process is considerably slower. This is due to the more rapid diminution in the specific surface of the particles with the rise in temperature.

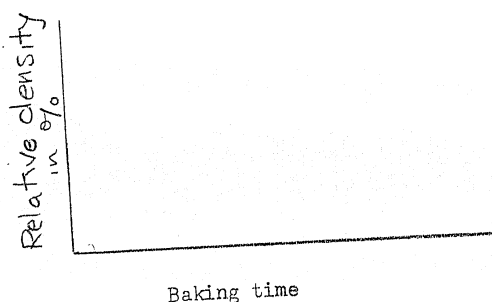


Figure 112. Ratio between shrinkage and the duration of the time-lag in baking at various temperatures (as per Kieffer and Hotop): 1. medium temperature; 2. high temperature.

The mechanical properties of a powdered metal change with the time-lag in baking approximately in the same manner as shrinkage and density. The strength of powdered metal (Figure 113) usually attains its maximum level rather rapidly. With the further time-lag, it remains at the level attained, or is even somewhat diminished. The properties, characterizing plasticity, as, for instance, elongation, most of the time grow over a much longer period (see Figure 113). This is due to the fact that

the full elimination of oxygen, as pointed out in the Offermann thesis (126), requires a rather long period of time (see Figure 114).

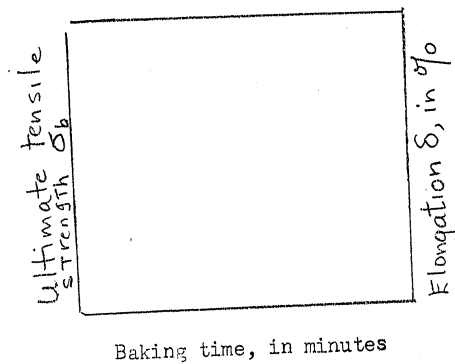


Figure 113. Ratio between ultimate tensile strength σ_b and elongation δ , on the one hand, and the time-lag in baking, on the other hand, -- in the case of vorticity-mill iron, 6 T/cm², 800 degrees centigrade (in accordance with Eilender and Schwalbe).

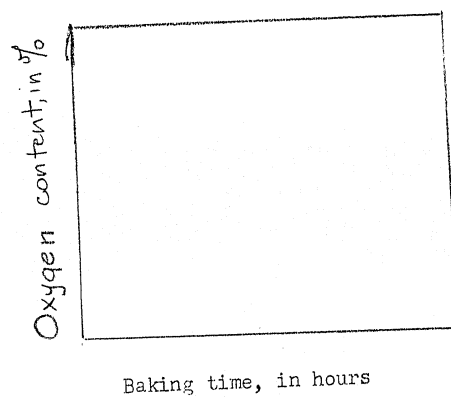


Figure 111. Ratio between the oxygen content and the baking time, in the case of carbonyl iron (in accordance with Offermann).

The ratio, at which the temperature rises, is reflected perceptibly in the mechanical properties.

A rapid rise is inevitably linked to localized differences in temperature, which may result in the local isolation of shrinkage and increase the non-regularized localization of individual changes in the particles. Therefore, density and other mechanical properties are lower in specimens that were heated rapidly. A rapid temperature build up may sometimes even result in flaws, such as buckling, overheating, non-uniform shrinkage, and the like.

As already indicated in Paragraph 71, the rate of cooling (if no phase transformations occur) may be of some importance only in the case of a short time-lag in the maximum baking temperature. In this case, a slow rate of cooling may sometimes result in a somewhat higher density and other mechanical properties.

73. The Effect of the Size, Shape, and Structure of the Particles

The specific surface of the powder particles and the number of contact points between them diminish with the size of the particles. Therefore, with the drop in the degree of dispersion of the powders, the effect of the processes, promoting the drawing together of the particles and the growth of contact,

is considerably reduced.

The strength of the briquettes (see Paragraph 47), with the increase in the size of the particles, is either reduced or remains without change. Therefore, in a number of cases, with a drop in the degree of dispersion, the effect of the processes, disrupting the contact, remains the same, or is even somewhat enhanced. The "macroscopicity" of the individual changes may at times increase the disruption of the contact. In heating up to 100 degrees centigrade, the thermal expansion of the particles amounts to about 0.1 percent. For particles of 1-millimeter size, deformation in this case amounts to 1 micron, and it may affect the disruption of the contact. For particles 1-micron in size, the absolute deformation amounts to 0.001 of a micron, and it may even be conducive to an increase in the contact between particles.

Thus, with the size of the particles, the effect of the processes, promoting the drawing together of the particles, is attenuated, while the effect of the processes, promoting the drawing apart of the particles, remains the same, or is even increased. Therefore, as a rule, shrinkages are diminished with greater sizes of the initial powder particles. At a certain predetermined size of the particles, shrinkage becomes equal to zero, after which it begins to increase. Alongside of this, all the mechanical properties are attenuated. The temperature at which visible shrinkage sets in is also somewhat reduced with the increase in the degree of dispersion of

the initial powders.

In the baking of dispersed powders, the contact surface of the particles grows considerably. In the case of coarse powders, the contact, formed in pressing, is frequently somewhat decreased in baking. In this case, the part played by baking is reduced primarily to the qualitative change in contact (the transition from a stressed to a non-stressed, and from a metallic to a non-metallic state).

At times, with a diminution in the degree of dispersion in the powders, the strength of the briquettes is increased. It being the case that the effect of the local isolation of shrinkage may also be diminished. If the effect of the processes of drawing the particles apart, with a reduction in dispersion, is diminished more rapidly than the effect of the processes drawing the particles together, which occurs in relatively rare cases, an increase in density and in the contact surface, and also a rise in the other properties of articles made from the coarser powders, result.

The increase in the pouring weight of the powders in most cases reduces shrinkage and mechanical properties. The increase in pouring weight frequently coincides with an increase in the size of the particles and with a diminution of the specific surface. But also independently of other factors, the pouring weight affects the results of baking. The pouring weight

characterizes the structural strength of the powders. With the increase in pouring weight of the powders, the strength of the briquettes is diminished, as a result of which the effect of the processes, promoting the drawing apart of the particles, is increased, while density and the contact surface of the particles, and also the mechanical properties of the articles, are diminished.

A considerable effect is exerted by the structure of the particles. The rougher particles have a greater specific surface, and they produce stronger briquettes, which promotes the obtaining of products of higher strength and density in baking. By the same token, angular particles are preferable to spherical ones (when baking briquettes, but not loosely poured powders). Particularly unfavorable results ensue from the baking of briquettes prepared from powders with flat particles, since such substances are easily disintegrated during the absorption of residual stresses.

The presence of internal subdivisions in the powder particles (carbonylic, electrolytic) is linked to the accelerated mobility of the atoms at the boundaries of these subdivisions and to internal recrystallization. This increases the rate of creep and stimulates the processes both of the drawing together and of the drawing apart of the particles (with the emphasis usually on the drawing together).

The presence of associations of particles is conducive

to the isolation of shrinkage (within the limits of these associations), and, therefore, somewhat reduces density and the other properties of the baked articles. However, the favorable effect of these associations of particles upon the properties of the briquettes may sometimes outweigh the above indicated negative effect.

In baking mixtures of powders, their volumes, also their volumetric and linear changes are additives of the properties of the initial components. Conformantly, the volume of a mixture is determined as follows:

$$V = V_1 + V_2 \quad (73/1)$$

where V is the volume of the mixture
 V_1 and V_2 are the volumes of the baked components.

The relative volume of the baked mixture is determined by formula:

$$\beta = \frac{n_1 \beta_1 + n_2 \beta_2}{n_1 + n_2} \quad (73/2)$$

where β is the relative volume of the mixture;
 β_1 and β_2 are the volumes of the components;
 n_1 and n_2 are the weight ratios of the components.

The volumetric shrinkages of the mixture vary in accordance with formula:

$$\frac{100 \Delta V}{V} = \frac{n_1}{n_1 + n_2} \frac{100 \Delta V_1}{V_1} + \frac{n_2}{n_1 + n_2} \frac{100 \Delta V_2}{V_2} \quad (73/3)$$

where $\frac{100 \Delta V}{V}$ is the percentage-wise change in the dimensions of the mixture after baking, etc.

The mechanical properties of the mixtures depart from the rule of additivity⁽²⁾.

Figure 115 is a curve graph in which the attenuation of mechanical properties in relation to the growth in the size of the particles of the initial powders is plotted, according to Eilender and Schwalbe.

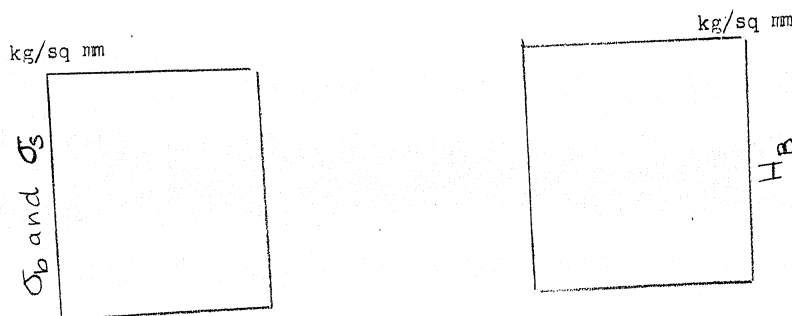


Figure 115. Ratio between the mechanical properties of baked vorticity mill iron and the particle sizes of the initial powders (in accordance with Eilender and Schwalbe):

I. particles < 0.075 millimeter; II. particles equal to $0.075 - 0.1$ millimeter; III. particles equal to $0.1 - 0.5$ millimeter; IV. particles less than 0.5 millimeter.

Figure 116 is a curve graph depicting the diminution in shrinkage, and Figure 117 is a curve graph depicting the attenuation of the mechanical properties in relation to the increases in

the pouring weight of the initial powders.

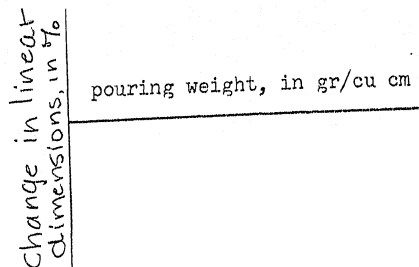


Figure 116. Ratio between the change in linear dimensions of iron powder briquettes and the pouring weight of the powder (initial porosity 36 percent, baking time 45 minutes, baking temperature 1100 degrees centigrade):

1. in a longitudinal direction;
2. in a transverse direction.

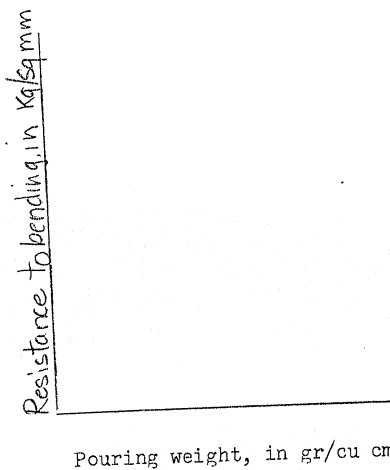


Figure 117. Ratio between the ultimate bending strength and the

pouring weight of copper powders (porosity of the briquettes 40 percent, baking time 45 minutes, baking temperature 800 degrees centigrade):

1. in a longitudinal direction;
2. in a transverse direction.

By analyzing the curve graph, plotted in Figure 116, deductions, relating to longitudinal and transverse shrinkages, can be made. In the case of powders with lower pouring weights (at any rate, with lower degrees of consolidation), the shrinkages in the direction of compression are greater than in a transverse direction, and the curve of the longitudinal shrinkages lies below the curve of the transverse shrinkages. Within the range of powders of high pouring weights, a reverse ratio is true. The paths of the curves, depicting the longitudinal and transverse shrinkages, resemble scissors (see Figure 118).

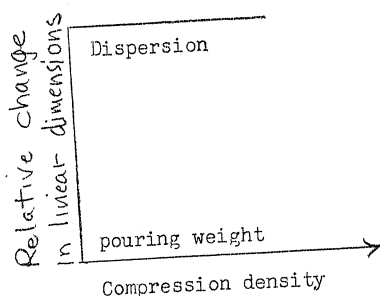


Figure 118: Diagram of the change in linear dimensions in baking:

1. in a longitudinal direction;
2. in a transverse direction.

This phenomenon is due to the following. The greater number of surface contacts is disposed in the direction of compression, as compared to the number of contacts disposed in a transverse direction. In the case of the fine particles, the processes of drawing together, manifesting themselves in the constriction of the particles to the surface of contact, predominate. Hence, the maximum increase in density will occur in longitudinal direction. In the case of coarse powders, the predominant processes are the processes of drawing the particles apart, which, in their turn, run in a direction normal to the contacts. As a result, this case will show less shrinkage (or greater growth) in the direction of compression.

A particularly great increase in longitudinal dimensions is observed in the baking of briquettes from powders with flat particles (the flat shape of the particles facilitates the disruption of the contact during the absorption of the residual compression stresses).

74. The Effect of the Size and Shape of the Particles upon the Structure of the Baked Products

The structure of a baked powdered metal (secondary structure) depends greatly on the structure of the briquette (primary structure).

The following regularities in the change of structure in baking, in relation to the structure of the initial powders,

are to be noted.

(1). The temperature at which the growth of particles begins is reduced, and the grain size of the baked metal is increased with the degree of dispersion of the initial powders. Table 54, compiled in accordance with the data by Agarkova and Korol'kov (1), shows the relation between the grain size of baked molybdenum and the particle size of the initial powders.

TABLE 54

[see next page]

This regularity is due to the following:

(a). As in the case of compact metals (see Paragraph 56), the rate of the growth of grain is increased in a direct ratio to the first or even a higher power of the degree of dispersion. Therefore, with the same time-lag, the visible growth of the fine particles will occur at a lower temperature. With the same temperature and time-lag, fine particles will grow to larger dimensions.

(b). A higher content of oxides and a low permeability of fine-particle briquettes are of some importance (see Paragraph 40).

(c). The processes of shrinkage promote the growth of the particle, the processes of drawing the particles apart hinder same. Fine powders show considerable shrinkage, coarse

TABLE 54

Change in the Size of the Grain in the Baking of Molybdenum
 (as per Agarkova and Korol'kov)

<u>Mean size of</u> <u>particles of initial powder</u>	<u>grains of baked metal</u>	<u>Mean number of grains</u> <u>per 1 sq mm</u>	<u>Power to which grain dimensions</u> <u>are raised in baking</u>
	22.0	2000	26.0
0.77			
	22.0	2000	22.0
1.00			
	19.0	3000	18.0
1.10			
	17.0	3600	11.0
1.49			
	15.8	4000	10.0
1.59			
	13.9	5000	6.5
2.10			

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powders show volumetric growth.

(d). The size of the pores is in proportion to the size of the particles. The large pores of the coarse powders cannot, and the small pores of the fine powders can, be closed up in shrinkage, or included in the grain during the growth of the latter (see Paragraph 71).

(2). In the case of fine powders, the temperature at which the growth of the grain begins sometimes depends on the compression pressure (see Paragraph 71).

(3). The temperature of the beginning of the growth and the size of the grain depend on the shape of the initial particles of the powder. For instance, collapsed flat particles show only a negligible tendency to growth. The growth of grain in briquettes from copper powders with flat particles begins only at 1000 degrees centigrade. This is due to the disruption of the contact between the flat particles during the absorption of the residual stresses. In articles made from such powders, the primary orientation of the particles is frequently preserved.

(4). The presence of submicroscopic subdivisions of the particles in most cases promotes grain growth.

(5). As already discussed in Paragraph 71, the change in the nature of porosity during the baking process --, the formation of closed and intraparticle pores, is characteristic of fine powders. Articles made from coarse powders retain the characteristics

of their porosity. In contradistinction to fine powders, coarse powders frequently retain their primary structure (the size and shape of the particles and pores, the preservation of the compression orientation).

(6). Baking, as a rule, cannot completely destroy the structural characteristics promoted by the preceding operations (screening, pressing) (see Paragraph 75).

75. The Effect of Compression Density

The processes of the growth of contact and the drawing together of the particles are primarily induced by the constriction of the atoms from the free sections of the surface to its contact sections (see Paragraph 62), and to some extent, by thermal expansion (see Paragraph 66).

Figure 119 is a diagrammatic representation of the contact conditions between two particles of a briquette. In pressing, only an incomplete contact along surface AA is attained. In heating, a complete contact along surface AA may be attained as a result of thermal expansion. This process may lead to a very considerable growth of the contact, but will practically not affect the density, since there is only a negligible translocation in the basic metal mass. On the other hand, the constriction of the atoms from the free surface BA and AA is linked to a considerable translocation of the metal and to great shrinkages. Thus, no substantial error will be admitted, if, in computing the shrinkage (but not the changes in contact),

the free sections of the surfaces AA are disregarded, and only the free surfaces AB are taken into account.

As a result of shrinkage, i.e., of the constriction of the higher-mobility atoms from the free sections to the contact sections of the surface, the number of these atoms is diminished, while the contact surface is increased. It is natural to make the first assumption that the diminution of the number of mobile atoms in shrinkage (or, which is the same, the diminution of the free surface) is in proportion to their initial number (the initial magnitude of the free surface). It being the case that, as was already indicated, an approximate determination of the magnitude of the surface is sufficient.

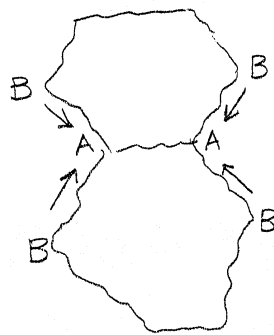


Figure 119. A diagram of conditions of contact between two particles in baking.

Let us compress two similar weighed batches of a powder to different degrees of porosity. The volume of the pores of

briquettes varies in proportion to the coefficient of porosity

ϵ (see Paragraph 14). Some authors are greatly in error, when they conceive of the pores as closed spheres, the surface of which is in proportion to the square, and the volume -- in proportion to the cube of the radius. In reality, the volume, the surface area, and the linear dimensions of communicating pores, all change in the same proportion. (see Figure 71).

"Individual" pores are restricted from different sides by the free surface of the particles (the solid lines in Figure 120). The entire surface of such pores, including the "empty" dotted-line surfaces, is in proportion to ϵ . The free surface of the particles (solid lines in Figure 120), which is of interest to us, is in proportion to $\sqrt{\epsilon}$, where $\sqrt{\epsilon}$ is the relative density of the briquette. The expression $\sqrt{\epsilon}$, in conformity with formula (14/6), equals the initial porosity Π of the briquette. In connection with this proportionality, the initial free surface may be substituted by Π , and its diminution through the diminution of porosity -- by $\Delta \Pi$ in the presence of shrinkage (or, which is the same, by the increase in relative density $\Delta \sqrt{\epsilon}$).

Then:

$$\Delta \Pi = \Delta \sqrt{\epsilon} = k \Pi, \quad (75/1)$$

where k is a constant coefficient.



Figure 120. Diagram for the computation of the surface of the pores.

Figure 121 is a curve graph depicting the relation between $\Delta \rho$ and Π for some powders. The analysis of the curve shows that, within a certain range of porosities, it approaches a straight line. Extending the rectilinear section of the curve until it intersects with the coordinate axes, we see that the straight line intersects the latter not at the zero point, but in accordance with the equation:

$$\Delta \rho = k \Pi - C, \quad (75/2)$$

where C equals the diminution in density (increase in porosity), with $\Pi = 0$.

Such translocation is stipulated by processes conducive to the drawing apart of the particles. The departures from rectilinearity in the area of low porosities are, seemingly, caused by the acceleration of the processes of drawing the particles apart. The sharp decrease in the growth of density and the inflexion of the curves at high porosities (on the order of 40 percent) cannot be explained by the drawing apart of the

particles only. To begin with, in the presence of low density, the free surface grows no longer in proportion to density, but to a very negligible extent.

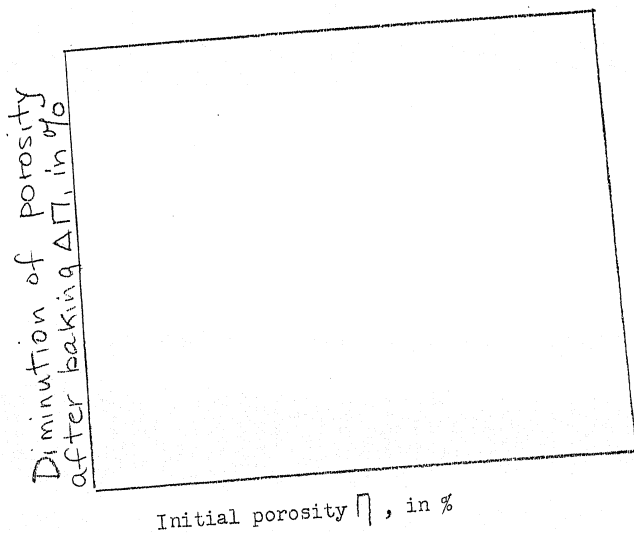


Figure 121. The relation between the initial porosity and its diminution (increase in relative density) in baking:

1. electrolytic copper powder, pouring weight 1.50 grams per cubic centimeter, 800 degrees centigrade, 45 minutes;
2. reduced iron powder, pouring weight 0.67 grams per cubic centimeter, 1100 degrees centigrade, 45 minutes.

In addition, the assumption of the existence of a direct ratio between the diminution of the free surface and its initial magnitude, is only on the order of a first approximation. Actually shrinkage depends greatly, in addition to the initial magnitude

of the initial surface, on the initial number of contacts in a unit of volume.

With complete absence of contact, for example, during the baking of particles, loosely poured upon a plate, no shrinkage can occur. With the increase in the number of atoms, which were in contact prior to baking, the rate of growth of new contact sections, forming by the constriction of the atoms to the already existing sections, must increase. Thus, powders, somewhat consolidated by shaking, practically always show a somewhat greater shrinkage in baking than freely poured powders. The density of the briquette is always greater in a longitudinal direction than it is in a transverse direction. Figure 122 shows that longitudinal shrinkages, in the presence of low densities of the briquettes, are greater than transverse shrinkages. Hence, in these cases, shrinkage grows not with a diminution, as it usually does, but with an increase in briquette density.

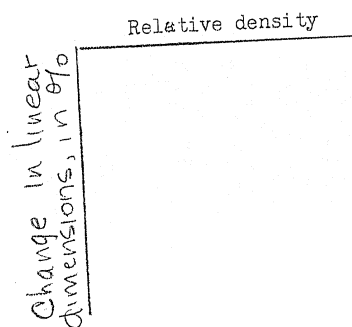


Figure 122. Ratio between linear shrinkage of electrolytic

copper powder (pouring weight 1.50 grams per cubic centimeter, baking time 45 minutes, at 800 degrees centigrade) and briquette density:

1. in a longitudinal direction;
2. in a transverse direction.

The places of contact act like pumps transferring atoms from the free sections. It is, therefore, natural to suppose that the diminution in the free surface ($\Delta \Pi$) is in direct ratio not only to the initial magnitude (Π), but also to the number of contacts in a unit of volume. In the first approximation, the density of the contacts in a unit of volume is in proportion to ϱ . Then:

$$\Delta \Pi = \Delta \varrho = k \varrho \Pi \quad (75/3)$$

or

$$\frac{\Delta \varrho}{\varrho} = k \Pi \quad (75/4)$$

The expression

$$\frac{\Delta \varrho}{\varrho} \approx \frac{\Delta V}{V_0} \quad (75/5)$$

where

ΔV is the reduction in volume in baking;

V_0 is the initial volume;

$\frac{\Delta V}{V_0}$ is the volumetric shrinkage.

Indeed

$$\begin{aligned} \frac{\Delta V}{V_0} &= \frac{\Delta \beta}{\beta} = \frac{\beta_1 - \beta_2}{\beta_1} = 1 - \frac{\beta_2}{\beta_1} = 1 - \frac{\varrho_1}{\varrho_2} = (75/6) \\ &= \frac{\varrho_2 - \varrho_1}{\varrho_2} \approx \frac{\varrho_2 - \varrho_1}{\varrho_1} \approx \frac{\Delta \varrho}{\varrho} \end{aligned}$$

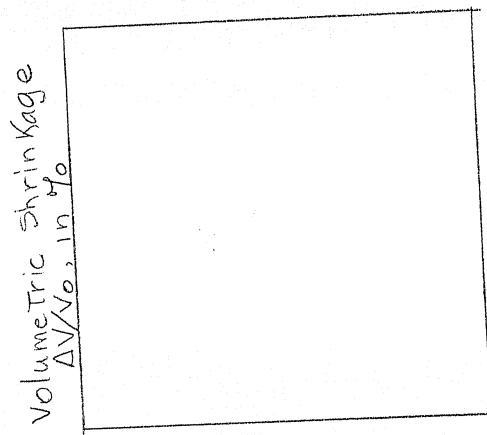
$$\frac{\Delta V}{V_0} \approx k \Pi$$

(75/7)

Figure 123 is a curve graph depicting the relation between shrinkage $\frac{\Delta V}{V_0}$ and the initial porosity for some powders. The curves in Figure 123 have a larger section of rectilinearity than the curves in Figure 121. Due to the same causes, the extension of the straight line intersects the coordinate axes not at the zero point, but in accordance with equation:

$$\frac{\Delta V}{V_0} = k \Pi - C, \quad (75/8)$$

where C is the growth in volume at zero porosity.



Initial porosity, in %

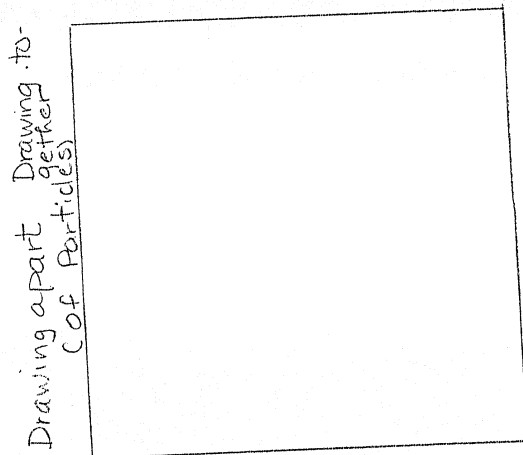
Figure 123. Relation between volumetric shrinkage $\frac{\Delta V}{V_0}$ and initial porosity of the briquettes (electrolytic copper, pouring weight

1.50 grams per cubic centimeter, 800 degrees centigrade, 45 minutes).

Let us give an approximate evaluation of the processes conducive to the drawing apart of the particles. The order of magnitude of constant C in formulas (75/2) and (75/8) usually corresponds to approximately a 5 percent growth in volume. This is a magnitude of the same order as the increase in volume induced by the full absorption of the compression stresses. Thus, it is rather probable that, in a number of cases, the growth is, to a considerable extent, induced specifically by the residual stresses. This growth (see Paragraph 43) depends little on density, and is, probably, somewhat increased in the presence of the maximum, and possible also of the minimum pressures. Zonality must (although for different reasons) be manifested at its maximum in the presence of the highest and the lowest densities. The negative effect of the individual changes in the particles (and, possibly, also of thermal expansion) is most perceptible at high densities. The bulging out effect of the gases, in the opinion of the author, is insignificant. Figure 124 shows a conjectural ratio between the effect of the various processes upon shrinkage and density. The character of this ratio may change considerably for different powders and for different baking conditions. The intensification in the effect of the processes, conducive to the drawing apart of the particles, in the presence of very small or very high porosities, is linked to a certain extent to the corresponding

reduction in the relative strength of the briquettes, expressed in terms of percentage of compression pressure (see Figure 69, curve 4).

In powders manifesting high shrinkages, the process of baking levels out considerably the differences in porosity between the products compressed to different densities as well as between the spots of different densities in the same briquette (see Figure 125). This leveling effect is increased with the increase in temperatures and in shrinkages. The same effect of density leveling induces distortions in the shape of briquettes with different densities in different places.



Porosity of briquettes (conjecturally, 8%)

Figure 124. Diagram of the effect of the various processes upon

shrinkage in relation to the density of the briquettes. Porosity is conjectural, with the subsequent reduction of the oxides in baking taken into account. Therefore, all the curves originate not at the point of zero porosity, but at some point above the latter (corresponding to zero porosity of the non-reduced briquettes):

1. "contact" shrinkage due to atomic mobility;
2. the effect of residual stresses, of zonal isolation, of the liberation of gases, and of the component of the effect of the oxides, which attenuates the strength of the briquettes and of the baked products;
3. the effect of the thermal expansion of the particles;
4. the component of the effect of the oxides which activates baking;
5. the resulting curve.

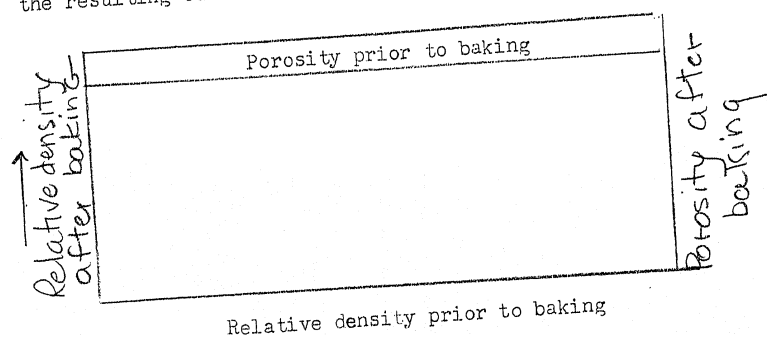


Figure 125. Relation between porosity and density after baking, on the one hand, and porosity and density prior to baking, on the other hand. Electrolytic copper powder, pouring weight 1.50

grams per cubic centimeter.

In the case of many powders in the medium ranges of compression densities, the final porosity after baking is approximately in proportion to the initial porosity. In the baking of powders with high shrinkages, rather numerous departures from this proportionality are observed. In that case, the final density is practically not dependent upon the initial density. The ratio of shrinkages in the case of highly-oxidized powders, and in a number of other cases, also departs from the usual type (see Figure 126).

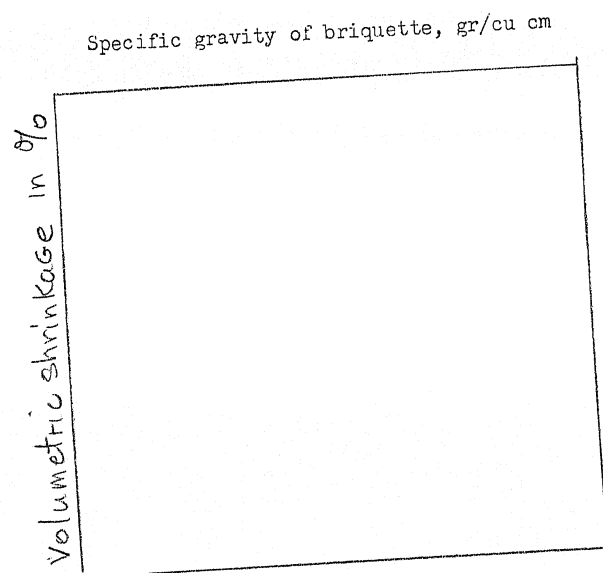


Figure 126. Shrinkage in copper briquettes (baking for 1 hour at 750 degrees centigrade):

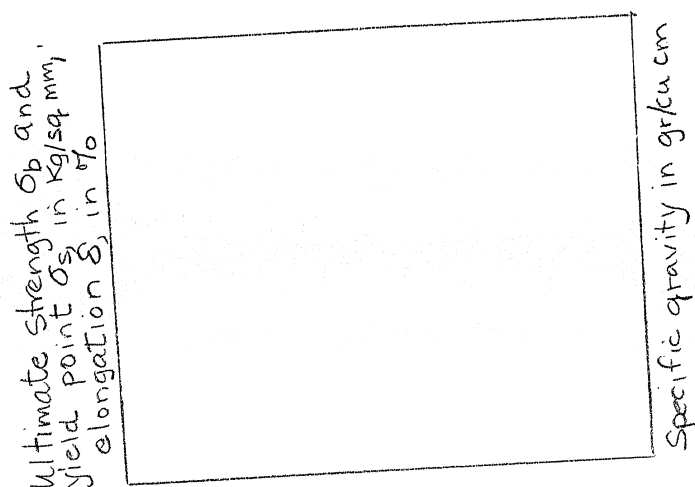
1. oxidized copper (1 percent of oxygen);
2. same copper powder prior to oxidation (0.1 percent of oxygen).

In Figure 122, the path of shrinkages in a longitudinal and transverse directions was already analyzed. The density of the contact orientation is greater in the direction of compression than in a transverse direction. In the presence of low densities, the increase in the area of previous contacts is predominant. Therefore, shrinkage in a longitudinal direction (i.e., in the direction of the maximum number of contacts) will be of a smaller magnitude. In the presence of high densities, on the contrary, there is a greater disruption of contacts and a greater growth in dimensions in the above direction. It is particularly necessary to take into account the fact that the absorption of residual stresses induces the maximum expansion in a direction perpendicular to the contacts, i.e., in a longitudinal direction.

The mean shrinkage value in briquettes of the same mean density depends considerably on the distribution of the latter. For instance, in the presence of high density in the center, and low density at the periphery of the briquette, shrinkage will be higher, than in an inverse distribution of density.

The mechanical properties of the products are enhanced with the density of compression (Figure 127). In powders with high shrinkage values, the leveling effect of baking results in the leveling of density and other mechanical properties in a progression with temperature. (see Figure 100). In some cases, even an attenuation of mechanical properties with compression density is observed (particularly when excessive pressures re-

sulted in flaws during the pressing operation). However, in most cases, the mechanical properties of highly-compressed products are higher even though the products, after baking, may have a somewhat lower density than the products not so highly-compressed. Particularly high is the growth, with pressure, of the contact surface, of the density, and of the other mechanical properties in the case of powders which show negligible volumetric changes as a result of baking.



Compression pressure in kg/sq mm

Figure 127. Ratio between density γ , yield points σ_s , ultimate strength σ_b , and elongation δ , on the one hand, and compression pressure, on the other hand, in the case of baked vorticity mill iron (800 degrees centigrade, 30 minutes) in accordance with the data by Eilender and Schwalbe.

It must be emphasized particularly that the structural effect, induced by compression, can never be completely balanced off in baking. Compression disintegrates the association of particles (when such exist) and fills the large pores. Compression resolves the skeleton strength of the material, as caused by the engagement and interlacing of the particles. Consolidation as a result of shrinkage in baking primarily increases the cohesion between, but not the engagement of, the particles, and fills the fine, but not the large pores. Hence, the process of baking can never fully compensate for the favorable structural changes, induced by high compression. It follows from this, that the obtaining of briquettes of the highest possible density should be aimed at. This possibility is restricted, on the one hand, by the wear in the press molds, and, on the other hand, particularly in the case of some powders, by unfavorable structural changes resulting from excessive pressure, such as lamellar fissures, which cannot be rectified in baking, and the excessive orientation of flat particles.

76. The Effect of the Preliminary Treatment of Powders

The mixing of powders in ball mills is accompanied by the following changes:

(1). As a result of the treatment, there occurs the breaking up of associations of particles, of the particles themselves, particularly in the case of brittle and hard metals, and of the surface layer of oxides on the particles.

(2). Alongside of the reduction size, occurs the reverse process of the diminution of the specific surface of the particles, due to the collapsing and the rolling up of roughnesses and protuberances, particularly in the case of soft and ductile metals.

(3). The surface oxidation of particles is possible.

(4). Treatment in the ball mills induces a cold-hardening effect in the particles.

(5). The flattening out of the particles, particularly in the case of soft and ductile metals, is possible.

(6). The disintegration of the surface layer and the collapsing of the particles reduce the strength of the powders and of the briquettes, as is indicated by the continuous increase in the pouring weight of most of the powders treated in ball mills. The cold-hardening of the metal also reduces the strength of briquettes.

Some of the above factors, such as the reduction in size of the surface layer of the particles, the breaking up of the associations of particles, stimulate the growth of the contact surface and the increase in shrinkage during baking. Other factors, such as the cold-hardening, the increase in the pouring weight, the decrease in the strength of the briquettes, and also the growth of the non-regularized localizations of the individual changes in the particles, promote

the disruption of contact and a reduction in shrinkages. Usually, at the beginning of the treatment in the ball mills, the positive factors (growth of shrinkages) predominate, as shown in Figure 128. Subsequently, the negative factors (diminution of shrinkages) take predominance.

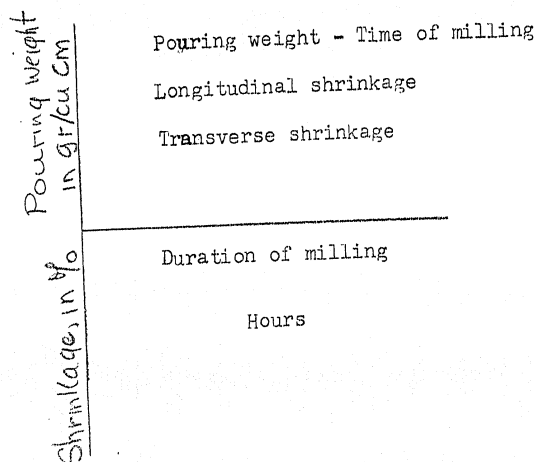


Figure 128. The effect of milling time in the ball mill upon the pouring weight of the charge and upon shrinkage in baking at 800 degrees centigrade -- for an electrolytic copper powder, with a pouring weight of 1.50 grams per cubic centimeter.

Preliminary annealing of the powders (prior to pressing) is linked to the following changes:

- (1). An increase in the strength of the briquettes in connection with the removal of the cold-hardening effect from the particles and with the diminution in the content of oxides

-- this phenomenon increases shrinkages.

(2). A diminution in the specific surface of the particles -- this process reduces shrinkage.

(3). An exhaustion of the capacity for individual changes in the particles. This process, by causing a reduction in the rate of creep, has a double effect of retarding both the drawing together as well as the drawing apart of the particles.

Annealing usually leads to positive results in the case when it produces greater strength in the briquettes (see Figure 73). In the opposite case, it may lead to negative results (Figure 129).

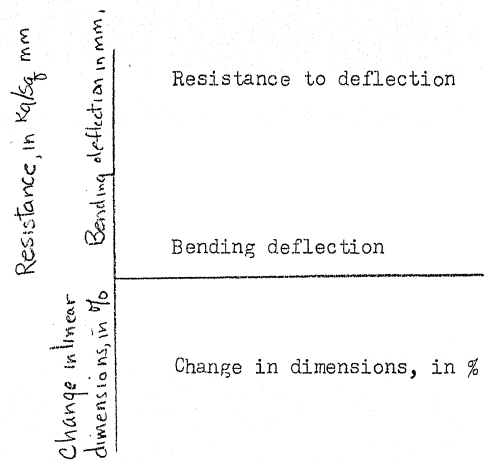


Figure 129. The effect of the preliminary annealing of an electrolytic copper powder upon the shrinkage and the mechanical properties of the baked products -- baking temperature 800 degrees centigrade:

1. ultimate bending strength;
2. bending deflection;
3. linear shrinkage.

77. The Effect of the Generic Classification of the Metal and of the Phase Transformations

In itself, the generic classification of the metal does not substantially affect the process of baking. In the case of all pure metals, all other conditions being equal, the same processes occur at the same respective temperatures. Thus, the third stage of baking, for all metals, begins at a temperature equal to 20 to 40 percent of the melting point (depending on the degree of dispersion, on the content of oxides, and their reducibility, and not on the generic classification of the metals), while the growth of the particles begins at a temperature equal to 60 to 75 percent of the melting point (again in relation to the degree of dispersion and the content of oxides).

The difference in the metal manifests itself in the process of baking only indirectly, inasmuch as it promotes differences in the strength of the briquettes (refractory and hard metals result in briquettes of lower strength), and in the reducibility of the oxides (for instance, the oxides of aluminum and zinc are difficult to reduce), and it may also be linked to the presence of phase transformations.

In iron, at the temperature of 910 degrees centigrade

there occurs the $\alpha - \delta$ -transformation which is linked to the increase in density during the heating of the compact metal, and a drop in density to its previous value in cooling. The density of porous iron, cooled to room temperature, after baking at a temperature somewhat higher than point Ac_3 , is somewhat diminished, due to the $\alpha - \delta$ -transformation (see Figure 130). Alongside the diminution in density, the mechanical properties of the porous metal are also attenuated. This diminution in density and mechanical properties sometimes continues also at a considerably higher temperature, up to 1100 degrees centigrade. The drop in the mechanical properties at the very point of transformation can also be explained, in accordance with Jones ⁽²⁷⁾, by the non-simultaneous transformation cycle in different particles, as a result of which the contact between them is disrupted, and density is reduced. However, the further reduction in density at higher temperatures, when transformation has definitely ended, can be explained only by the intensification of the effect of the processes of the non-regularized localization of individual changes and of the isolation of shrinkage, induced by phase recrystallization. This opinion of the author of this book ⁽⁷⁾ is supported by the Bryukhanov thesis ⁽²²⁾, based on the investigation of the recrystallization textures. The above thesis maintains that recrystallization and the visible change in the orientation of the grain occur only with a relatively prolonged heating at a temperature above the point Ac_3 .

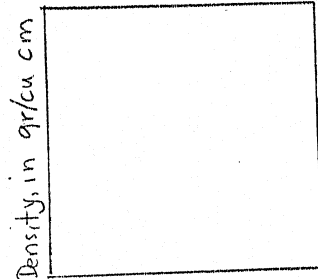


Figure 130. Ratio between the density of iron and the baking temperature (as per Sauerwald).

78. Investigation of the Individual Changes in the Particles in

Baking

Eleven years ago, the author of this book investigated in one of his publications ⁽⁸⁾ the changes taking place in the powder particles during the process of baking. Various powders were annealed at various temperatures under various time-lags. Upon cooling, the volumetric characteristics (the pouring weights) were measured, and, in some cases, the measurements of adsorption were taken (Footnote. The German scientist Hüttig, in a number of articles ⁽¹⁰⁵⁾, published during the war, furnished data analogous to the data previously arrived at by the author of this book. He used the same methods, without referring to the author of this book). Figures 131 and 132 are curve graphs depicting the ratio between the volumetric characteristic, on the one hand, and the temperature and the time of annealing, on the other hand.

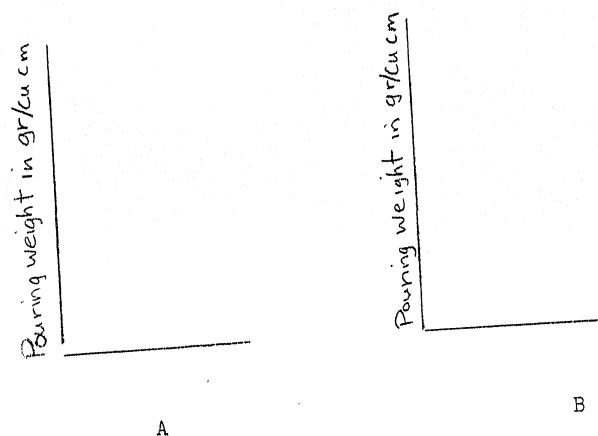


Figure 131. The change in volumetric characteristics of powders with the temperature of annealing:

1. electrolytic copper, pouring weight 1.5 grams per cubic centimeter;
2. same, compressed;
3. copper ore concentrate slime;
4. reduced iron, pouring weight 0.67 grams per cubic centimeter;
5. electrolytic iron, pouring weight 2.11 grams per cubic centimeter;
6. same, compressed;
7. electrolytic iron, pouring weight, 3.66 grams per cubic centimeter;
8. same as above, compressed.

The author obtained the following results:

- (1). At low temperatures on the order of 150 to 200 degrees centigrade, in the case of both metallic and non-metallic powders, obtained at room temperatures (by electrolysis,

mechanical disintegration), the diminution in the pouring weight (the increase in pouring volume) begins.

(2). In the case of powders freshly obtained at high temperatures (for instance, reduced powders), their characteristics do not change after annealing at a temperature below that at which they were originally prepared.

(3). The diminution in the pouring weight (the increase in pouring volume), with the rise in temperature, goes on continuously until a minimum pouring weight is attained. This point of inflexion corresponds, in the case of fine powders, to 40 to 60 percent of the absolute melting temperature of the metal, and, in the case of coarse powders, to 60 to 75 percent of the same. In coarse powders, the changes in pouring weight, are generally little perceptible.

(4). The point of inflexion is displaced in the direction of the lower temperatures, with the fineness of the powder and under the effect of the preceding cold-treatment. For instance, electrolytic copper of a pouring weight of 1.50 grams per cubic centimeter attained its point of inflexion at 500 degrees centigrade; after pressing at 25 kilograms per square millimeter and crushing, its point of inflexion was attained at 350° C; after pressing at 40 kilograms per square millimeter and crushing, its point of inflexion was attained at 300 degrees centigrade.

(5). After the point of inflexion has been attained, the pouring weight of the powder begins to increase (the pour-

ing volume begins to diminish). This range of temperatures can be divided into two parts.

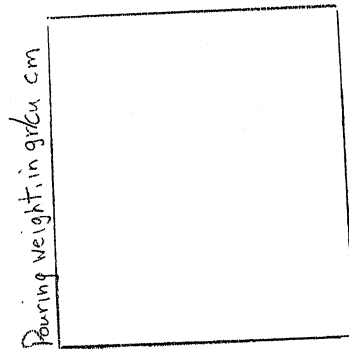
(a). The temperature range within which the pouring weight still does not exceed (or exceeds only to a negligible extent) its initial value prior to annealing. For instance, in the case of electrolytic copper with a pouring weight of 1.50 grams per cubic centimeter, the temperature of 600 degrees centigrade lies above the point of inflexion, but the pouring weight has not yet attained its initial value. In this case, the pouring weight-time ratio curve shows a continuous drop in pouring weight with the time-lag at 600 degrees centigrade (see Figure 137) [should read -- see Figure 132].

(b). The temperature range, within which the pouring weight exceeds its initial value and increases continually with the time-lag of annealing. For electrolytic copper with a pouring weight of 1.50 grams per cubic centimeter, this temperature range begins at 700 degrees centigrade (about 70 percent of the melting point), see Figure 132.

(6). The beginning of the temperature range, in which the pouring weight exceeds its initial value and continuously increases with annealing, does not depend on the preceding cold-treatment.

(7) Under low annealing temperatures, approximately on the order of 30 to 40 percent of the melting point of the metal,

as shown by adsorption measurements ⁽²⁾, the specific surface is greater than its initial magnitude (both for metallic powders and for oxides).



Time of annealing, in minutes

Figure 132. The change in the volumetric characteristics of powders in relation to the duration of annealing:

1. electrolytic copper, pouring weight of 1.42 grams per cubic centimeter, annealing at 700 degrees centigrade;
2. electrolytic copper, pouring weight of 1.58 grams per cubic centimeter, annealing at 600 degrees centigrade.

The above results are due to the following.

All the powder particles are like planets in miniature. Their upper layer is covered with moist fragments of oxides, which are in a sort of argillaceous state. At the temperature of about 150 degrees centigrade, the water boils out from the fine capillaries, with an accompanying shrinkage of the type

occurring in the desiccation of clay. It being the case that the surface layer of the particles becomes toughened, as a result of which the pouring weight of the powder is reduced. In the moist layer of oxides, the water closes the pores; in the desiccated layer, the water boils out from the capillaries, which thus become more accessible to the substance being adsorbed. This explains the increase in the pouring weight and in the specific surface of the metals and oxides at the temperature of about 150 degrees centigrade (corresponding to the first stage of baking, see Paragraph 70).

In the heating of metal powders above 200° centigrade, an important part is played by the reduction of oxides. As a result, the surface layer becomes tougher, and the pouring weight is more and more diminished. Adsorption measurement, may sometimes show, at this stage, an increase in adsorption due to the following causes.

(1). Metals have greater adsorption capacity than their oxides.

(2). The specific surface can actually increase. It is common knowledge that successive oxidation and reduction at low temperatures considerably enlarges the surface of a powder.

(3). In addition, the surface of the particles may become somewhat increased in heating, even apart from the process of reduction. This, by no means, contradicts the

second law of thermodynamics. Thus, the surface of a burnished metal plate becomes enlarged and rough in annealing. But the entire surface of the plate, including the internal surface of the grains, is thereby decreased. This stage corresponds to the second and, possibly, to the third stage of baking.

The appearance of a point of inflexion (at 40 to 60 percent of the melting temperature, in the case of fine powders), the increase in the pouring weight, which, as yet, is not attaining its initial values, and the decrease, at this stage, of the specific surface is due to the following. With a rise in temperature, the process of the reduction of oxides progresses, and the surface protuberances, although having become toughened (they do not fracture under brittle deformation), yield more easily to plastic deformation. Therefore, the pouring weight is greater than the minimum, even though not yet in excess of its initial value. With the time-lag the baking of the fragments and protuberances takes effect, and the surface layer becomes less porous and gains strength. The rise in the strength of this layer results in the diminution of the pouring weight with the time-lag duration in annealing.

At the following stage (about 70 percent of the melting point), the baking effect is increased to the point where it levels out the large protuberances and depressions in the surface of the particles. In addition, the surface layer is softened as a result of the complete elimination of the oxides. The

diminution of roughness and hardness grows with the temperature time-lag, and the pouring weight grows continuously with the duration of annealing. This stage is also characterized by a considerable diminution of the specific surface of the particles. These phenomena correspond to the end of the third and the beginning of the fourth stage of the baking process.

79. The Effect of the Baking Atmosphere

Baukloh and Henkel (80) experimented with the baking of the burnished surfaces of compact metals in vacuum and in an atmosphere of hydrogen. They cut the tensile strength test specimens into two halves, burnished the surfaces of the cut, clamped the two halves together in a special clamp, and baked them. The results are given in Table 55.

[see next page for Table 55]

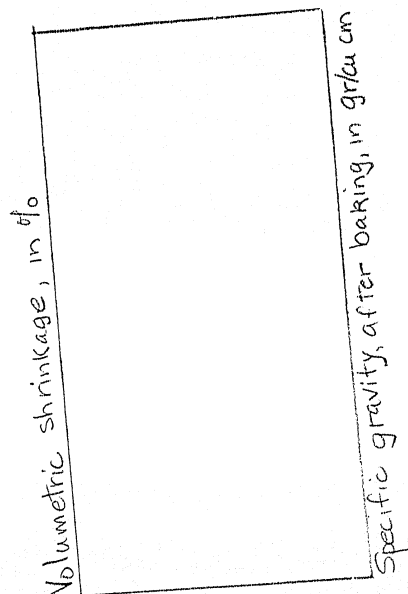
It can be seen from Table 55 that, in most cases, baking in vacuum began at lower temperatures and resulted in stronger contacts.

Figure 133, in accordance with Hetzel, depicts the density and the shrinkage for copper powder specimens, compressed under the same conditions and baked in vacuum and in hydrogen.

TABLE 55

The Effect of the Baking Atmosphere upon the Temperature at the Beginning of
Baking and upon the Maximum Strength Attained (as per Baukloh and Henkel)

Metals	Temperature of the be- ginning of baking in °C		Maximum strength attained, in kilograms per square millimeter		
	in vacuum	in hydrogen	temperature of baking in °C	in vacuum	in hydrogen
Al - Al	310	450	600	4.0	2.0
Cu - Cu	500	600	900	14.5	10.0
Cu - Ni	540	410	900	8.5	10.0
Steel - iron	550	600	1000	15.0	12.0
Cu - Fe	540	410	900	17.0	19.0
Steel	550	600	1000	20.0	25.0
Fe - Fe	550	600	1000	20.0	28.0
Fe - Ni	550	600	1000	19.0	22.0
Ni - Ni	550	600	1000	23.0	19.0



Compression pressure, in kg/sq mm

Figure 133. Ratio between the density of copper and the baking atmosphere (as per Hetzel):

1. shrinkage in vacuum;
2. shrinkage in hydrogen;
3. specific gravity in vacuum;
4. specific gravity in hydrogen--
baked for 16 hours at 750
degrees centigrade.

The author explains these results in the following manner.

- (1). The process of the formation of the new contact surface and shrinkage may be conceived as a sort of impregnation

of the pores by the mobile semiliquid surface layer of particles (see Paragraph 71). The presence of air makes the impregnation difficult, a vacuum facilitates the filling of the difficultly accessible capillaries. By the same token, the gas-containing intraparticle pores, as indicated by Frenkel' (64), cannot be filled completely with metal. Therefore, although the elimination of oxides is more rapid in an atmosphere of hydrogen, shrinkage and the formation of a new contact surface usually begin at a lower temperature and attain greater dimensions in vacuum. In mildly compressed copper powder specimens, the formation of the new contact surface is of great importance, and a vacuum produces better results than an atmosphere of hydrogen. In the case of highly compressed specimens, the formation of a new contact surface in baking is of no importance, and an atmosphere of hydrogen results in a density that is just as suitable.

(2). In some cases, importance is attached to the greater degree of freedom of the metal from admixtures in vacuum-baking (an improvement in density and other properties occurs) and to the slower and more difficult rate of the elimination of oxides in vacuum (density and other properties become deteriorated).

CHAPTER XI

THE BAKING OF MULTI-COMPONENT POWDERS

80. General Notes.

In the baking of powder metals consisting of several components, the following cases may occur:

(1). The components do not form, at the given baking temperatures, any solid solutions or chemical compounds in practically perceptible quantities.

(2). The components are reciprocally soluble under the conditions of baking, with no formation of a liquid phase.

(3). The components are reciprocally soluble under the conditions of baking, with the formation of a liquid phase.

As an example of the first case, copper-graphite and bronze-graphite compositions can be pointed to (Footnote. In this case, bronze is considered as a grouping of components (copper, tin), which are inert with relation to graphite). The baking in solid phase, in the presence of reciprocal solubility of the components, is exemplified by the baking of copper-nickel, iron-nickel, and other alloys. The baking with the formation of a liquid phase, in the presence of reciprocal solubility of the components, can be exemplified by the baking of the hard alloys (WC + TiC + Co, and others), of the so-called heavy alloy (W + Ni + Cu), etc.

Some cases do not fit within the framework of this classification. For instance, the combination iron-graphite may be considered as a case of reciprocal non-solubility of the components, when the graphite does not react under the conditions of baking, with the iron. Very frequently, however, cementite is formed during the baking of iron-graphite briquettes, and the system, then, must be considered as a case of reciprocal solubility. The same is true of the system copper-lead. In some cases, the copper reacts with the lead, in other cases, the system, to all practical purposes, can be considered as a case of reciprocal non-solubility.

81. The Case of Reciprocal Non-Solubility of the Components

The properties of a powder metal with full reciprocal non-solubility is primarily determined by the component entering into the charge in maximum volumetric quantity. Hence, the mechanical properties and density in conformity with the data analyzed in Chapter X, will improve with the degree of dispersion of the basic metal. A typical example of complete reciprocal non-solubility is the system copper-graphite. The effect of the inert component, entering into the charge in a smaller quantity (in this case, graphite), reduces itself to the following (see Figure 134).

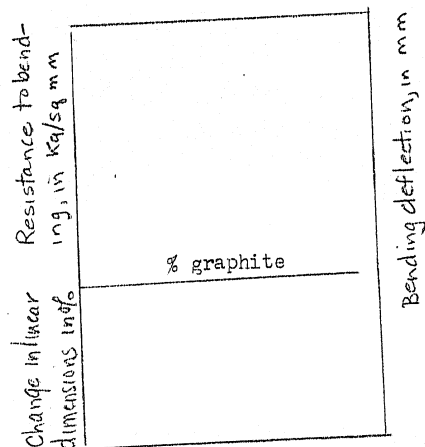


Figure 134. Relation between shrinkage and the mechanical properties of copper-graphite compositions and their graphite content (baking conditions -- 800 degrees centigrade, 45 minutes, 35 percent porosity):

1. change in dimensions in a longitudinal direction (electrolytic copper powder, pouring weight 1.50 grams per cubic centimeter;
2. same as above, except in a transverse direction;
3. ultimate bending strength, fine copper powder, pouring weight 0.64 gram per cubic centimeter;
4. ultimate bending strength, medium copper powder, pouring weight 1.50 grams per cubic centimeter;
5. ultimate bending strength, coarse copper powder, pouring weight 2.47 grams per cubic centimeter;
6. bending deflection, fine copper powder;
7. bending deflection, medium copper powder;
8. bending deflection, coarse copper powder.

(1) The graphite isolates, to a certain extent, the metal particles from mutual contact, hinders the constriction of the atoms to the places of contact in shrinkage, and thus counteracts the drawing together of the particles. The same isolation of contact attenuates the mechanical strength of the powder metal and enhances the effect of the processes which draw the particles apart and disrupt the contacts between them. Hence, the result of introducing graphite is a reduced shrinkage (frequently there is even a growth in dimensions as a result of baking). It being the case that, as was to be expected (see Paragraph 75), the longitudinal shrinkages diminish to a greater extent than the transverse shrinkages.

(2). The isolation of the metal particles from mutual contact grows with the amount and the degree of dispersion of the graphite. Hence, the diminution of shrinkage progresses with the amount and the degree of dispersion of the graphite.

(3). In most cases, the presence of graphite attenuates the mechanical properties and plasticity, it being the case that the degree of attenuation of the properties increases with the amount of graphite.

(4). In some cases, the introduction of graphite (in a small quantity, in the presence of an adequate degree of dispersion of the basic metal) induces, alongside of the diminution of shrinkage and density, a seemingly paradoxical increase in mechanical strength and deformability. This is due to the

increased homogeneity of the density distribution in the briquette with the introduction of graphite (see Figure 55), as a result of which the distortions in shape, buckling, and internal stresses are diminished after baking. At times, graphite also exerts a favorable deoxidizing effect.

(5). With the diminution of the degree of dispersion of the basic metal, the isolating effect of graphite upon the surface of the particles and its negative effect upon the mechanical properties grows. It is for this reason that the introduction of graphite into coarse metalloceramic charges is avoided.

(6). The ratio between the mechanical properties and the degree of the graphite dispersion is a very complex one. In the case of fine powders of the basic metal, best results are usually obtained by introducing a graphite of greater dispersion, even though it reduces shrinkage to a greater degree. The diagram (in Figure 135) explains such behavior on the part of the graphite. Fine graphite, disposing itself in the pores between individual particles, does not obstruct the contact between the latter, while coarse graphite creates a considerable local isolation of a series of particles. In the case of coarser powders, on the contrary, a coarser graphite, which in this case disposes itself in the interparticle pores, produces better results. While fine graphite isolates completely the surface of the particles, which has an extremely negative effect upon the mechanical properties. Thus, a certain commensurability

in the magnitude of the particles, as between the graphite and the iron, is necessary.



Figure 135. Diagram of the disposition of graphite:

a. fine graphite; b. coarse graphite

(7). The graphite has no substantial effect upon the temperatures of the beginning of shrinkage and the beginning of particle growth. In those cases, when the introduction of graphite resulted, during the baking process, in a considerable growth of porosity, some diminution of grain size was observed.

(8). A part of the graphite burns out in baking. The rate of burning out increases with general porosity and with the size of individual pores.

(9). Copper-graphite charges should be mixed in drums, and not in ball mills, to avoid the complete isolation effect.

The deductions drawn with reference to copper-graphite compositions may be extended also to other systems. For instance, the study of iron-graphite materials has shown that, even when the graphite reacts with iron, with the formation of perlite and cementite, this system is subject to the same regularities (only somewhat more complex) as a result of the

carburization of the iron).

To some extent, the results obtained in the study of copper-graphite compositions can be extended to the baking of metal powders containing inert admixtures disposed in the surface of the particles, or constituting general mechanical impurities.

The non-soluble components which are liquefied in baking, exert a somewhat different effect. At low briquette densities, the liquefied component may be completely transferred from the contact apertures into the large pores without hindering the contact of the particles of the refractory metal. In some cases, there will even be an increase in shrinkages, due to the increase in actual porosity at the expense of the volume of the liquefied component (the greater the porosity, the greater the shrinkages), or at the expense of some surface tension, created by the liquid phase. In the presence of considerable briquette densities, the liquid component isolates the contacts and greatly reduces shrinkage. For instance, one of the methods of obtaining iron sealing compounds of high porosity consists in the tight compression of a mixture of powders of iron and soda, with subsequent baking at a temperature of 1000 to 1100 degrees centigrade. The liquefied soda retards the drawing together of the iron particles. After baking, the soda is washed out from the pores. The temperature of the beginning of the particle growth remains the same, but the growth of the particles is considerably attenuated. Figure

136 is a curve graph depicting the considerable increase of shrinkages at low briquette density, and, inversely, the considerable reduction of shrinkages at high briquette density, in the case of the system copper-lead, by comparison with the initial copper. However, it is not completely clear as to what extent the system copper-lead may be considered, under the conditions of baking, as reciprocally non-soluble to all practical purposes. The accelerated growth and the characteristic shape of the grain (see Figures 84 and 143), which were observed in some cases, can be explained only by some degree of solubility of the copper in the liquefied lead. The baking of such systems is also made more complex by the phenomena of liquation of the fused components.

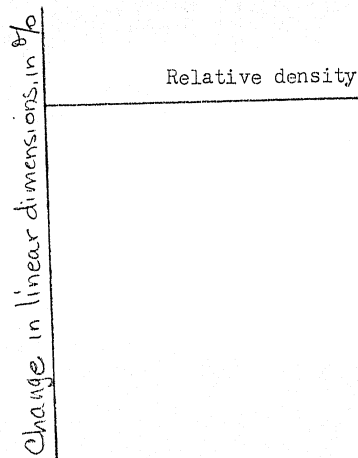


Figure 136. Ratio between the shrinkage of copper-lead specimens and compression density:

1. in a longitudinal direction;
 2. in a transverse direction
- (25 percent lead, 75% copper, baking temperature at 800 degrees cen-

tigrade, for 45 minutes).

82. Powders with Reciprocal Solubility of Components. Preliminary Remarks

First of all, it is necessary to clarify the basic differences between the single-component and multi-component powder metals in the case of reciprocal solubility in baking, in the absence of a liquid phase.

In the baking of powder mixtures, the visible formation of solid solutions or chemical compounds begins at a point below the melting temperature of the initial components, or their compounds and solid solutions. Schpring already indicated that, during the baking of compressed filings, diffusion processes are observed between the solid components, it being the case that pressure promotes diffusion. This deduction was later reaffirmed on the basis of micro-research, thermal analysis, and electrical conductivity measurements, by Mazing, whose work was abstracted into the Russian language in the book by Tammann "Metallography" (60).

The rate of reciprocal diffusion for two non-homogeneous metals is always considerably higher than for "auto-diffusion" of the atoms of the same metal. Therefore, an erroneous impression may at first be created that, if, during the baking of powders of various metals, atomic mobility is increased, much greater shrinkage and growth of the contact surface

should be expected than in the case of pure metals. However, Sauerwald (131) established that, in reality, shrinkages and mechanical properties of specimens baked from mixtures of powders Cu-Ni, Fe-Ni, and Cu-Fe, were always lower in value than the same computed in accordance with the rule of additivity, by the shrinkages and the mechanical properties of the initial components.

There are two basic reasons for these lower values.

(1). If mobility, in the presence of the diffusion of the atoms of two reciprocally-soluble metals is greater than the mobility of the atoms of one and the same metal, a reverse ratio is observed for the products of this reciprocal action, the solid solutions and the chemical compounds. Usually the addition of even a negligible amount of components, entering into a solid solution or forming chemical compounds, reduces the value of the surface tension of the basic component. Already by this alone, the assumption may be made about the diminution of the shrinkage-promoting interatomic forces during the formation of solid solutions. A considerable drop in the melting point, with the addition of admixtures entering into the solid solution, also points in the same direction. It would be erroneous, by proceeding from the increase in strength in the formation of solid solutions, to conclude that the forces of cohesion were enhanced. The growth in the strength of the solid solutions is stipulated primarily by the reduction in the mobility of the atoms in the formation of the unwieldy structural complexes and the complications in the

lattice structure. The reduction in mobility is reflected in a substantial rise in the temperature of recrystallization, with the entering of the admixtures into the solid solutions (regardless of the drop in the melting point). The same reduction in mobility causes a diminution of the rate of creep in most of the solid solutions, as compared to pure metals. Thus, in the baking of powders, in which solid solutions were formed even prior to baking, shrinkages and grain growth should be smaller than in pure metals, in connection with the diminution of the surface forces (surface tension) and the increase in the stability to creep, as compared with pure metals. While in the baking of powder mixtures, in which the reaction between the metals was not yet complete, the rate of shrinkage will rapidly become less than the rates of shrinkage in the case of pure metals, since the more active atoms in the surface of the particles form solid solutions even at the beginning of the baking process.

(2). The process of isolated shrinkage is no less, if not more, important in the case of multiple-component powders. Let us consider the baking process for a briquette made from a mixture of copper and nickel powders. Practically, with the intermixing of copper and nickel powders not being too perfect, the following combinations take place at various places in the article:

- (1). the contact copper-to-copper
- (2). the contact nickel-to-nickel

- (3). the contact copper-to-nickel
- (4). the contact hard solution-to-hard solution
- (5). the contact hard solution-to-copper
- (6). the contact hard solution-to-nickel

We called off only six types of various contacts, but there are considerably more of them, since the solid solutions have various concentrations. All these types of contact result in different degrees of shrinkage. Account must also be taken of the fact that not only is the chemical composition reflected in the shrinkage, but, vice-versa, the shrinkage is reflected in the chemical composition. Let us suppose that at a certain spot in the product an accelerated shrinkage and growth of contact between the particles of copper and nickel are setting in. This will lead to an acceleration of diffusion at this spot, since diffusion can only proceed through the contact sections. The formation of a solid solution, in its turn, will change the further rate of shrinkage. The difference in shrinkage at individual spots results not only in the formation of sections of different density, but also to a total diminution of density throughout the volume of the metal (see Paragraph 64).

It follows from the above that the non-uniformity of shrinkage is more detrimental in the case of powder alloys than it is in the case of pure metal powders, particularly when the intermixing is poor. This specifically is the reason the powders are sometimes mixed in ball mills over a 5-day

period.

A basic question arises as to which is the more efficient method -- whether to homogenize the mixture of the several powder metals by preliminary annealing, and then compress and bake the already homogenized particles, or to compress and bake the mixture of the pure metal powders as is.

In the opinion of the author, each of these methods has its advantages and its shortcomings, and one of them is to be preferred not on general principle, but only by taking into account the particular characteristics of each individual case.

The advantage of using an already homogenized charge is the homogeneity of shrinkage and composition. The disadvantages of this method are the difficulties in obtaining strong briquettes (the hardness of the homogenized solid solution is greater than the hardness of the initial components), and the exhaustion of a considerable part of the atomic mobility as a result of preliminary diffusion.

If it is necessary to obtain a rather porous alloy, it may be advantageous to use the non-annealed mixture of powders. For instance, according to the data by the author ⁽²⁾, the preliminary annealing of a charge made up of Cu-Ni and Cu-Fe powders, resulted in smaller shrinkages and attenuated mechanical properties, as compared to the products made from the non-annealed charges (porosity of briquette 30 percent). When

necessary to obtain almost compact materials (with no additional treatment after baking), the use of the homogenized charge is sometimes preferable. Thus, in the preparation of tungsten-titanium hard alloys, the preliminary annealing of the mixture of tungsten carbide and titanium carbide is frequently resorted to.

83. Powder Mixtures with Reciprocal Solubility of Components --

Further Data

The basic regularities in the baking of multi-component powder mixtures, in the absence of a liquid phase, are as follows.

(1). Shrinkage, the change in the contact surface, and the mechanical properties of the multi-component powders are usually subject to the same regularities as were discovered in the case of single-component mixtures, i.e., they also change with the degree of dispersion of the powders of each of the components, with compression density, with temperature, with the time-lag, and the like. If preliminary homogenized powders are used, baking can be considered, in principle, as a case of a single-component system.

(2). The rate and the completeness of the formation of solid solutions and intermetallic compounds increase with the degree of dispersion of each of the components.

(3). The method of mixing the charge is very important.

Intermixing in ball mills promotes closer contact between the particles and is conducive to the diffusion processes to a greater degree than mixing in drums.

(4). The increase in the density of the briquette increases the contact surface of the particles and accelerates the flow of the diffusion processes.

(5). Shrinkage and the change in the contact surface in baking exert an effect upon the diffusion processes. In the shrinkage of large articles during the process of baking, the maximum shrinkage stresses, and also the maximum density and contact surface dimensions occur in the central zone, in which, therefore, the formation of solid solutions and intermetallic compounds occur with maximum completeness.

At times the maximum completeness of reciprocal action between the components is also observed in the central zone with the expansion of the products as a result of baking, when the maximum value of the tensile stresses are concentrated in this zone. It is possible that, in this case, diffusion is accelerated due to the presence of stresses and the considerable displacement of the contact places in baking.

(6). The number of components that have reacted grows with the temperature and the duration of baking.

(7). Certain admixtures inhibit diffusion. Thus, according to the author, the carburizing of iron begins only at the temperature of 1000 to 1100 degrees centigrade,

and after a rather complete reduction of the oxides contained in the initial powders. The rapid reduction of the remaining oxides occurs at a point two-thirds to three-fourths of the absolute melting temperature of the metal. Thus, this temperature is not only the temperature at which the visible growth of the grain begins, but, in some cases, the temperature of the beginning of visible diffusion.

(8). Certain admixtures considerably accelerate diffusion. According to Offermann (126), negligible admixtures of sulfur and phosphorous promote the interaction between carbon and iron in the production of carbonyl steel. In all probability, this effect is due to the formation of eutectoids, which, in smelting at the baking temperature, increase the contact between the particles and accelerate the mobility of the surface atoms of iron entering into solution, as a result of which diffusion is intensified.

If the diffusion processes are effected through a gaseous phase, the composition of the latter is important. For instance, iron-graphite products, when baked in an atmosphere of dry hydrogen, are more strongly carburized than in an atmosphere of moist hydrogen. Of great importance is the gas-permeability which increases with total porosity and with the size of individual pores. The gas cementation of products made from coarse powders with greater porosity is effected more rapidly and completely than in the case of fine powders

with less porosity. The burning out of carbon is also more rapid in the baking of briquettes made from coarse powders.

The above described factors may be the underlying causes of non-homogeneity in the density of the structure, composition and mechanical properties even in the presence of uniformity in mixing and compression. In actual production, non-uniformities in mixing and compression play an important part.

Let us examine some examples of non-uniformity. Figure 137 (in accordance with Offermann (126)), which is a combination of a curve graph diagram and a corresponding micro-photo of zonality, depicts the chemical composition, density, and structure in the various zones of an ingot baked in an enclosed box from non-compressed powders of carbonyl iron containing about 1 percent of carbon and oxygen, respectively, with the addition of 1.2 percent of gas soot. The macro- and micro-structural examination showed the presence of four concentrically disposed zones: the first and the third with hypo-eutectoidal, and the second and the fourth with hyper-eutectoidal structure. Offermann ascribes this zonality to the effect of the gas atmosphere in the baking process.

However, if Offermann's viewpoint is accepted, the third zone should contain more of the chemically combined and less of the free carbon than the fourth zone, since the third zone is disposed in the more favorable conditions with

relation to gaseous exchange. Actually the third zone contains less chemically combined and more free carbon.

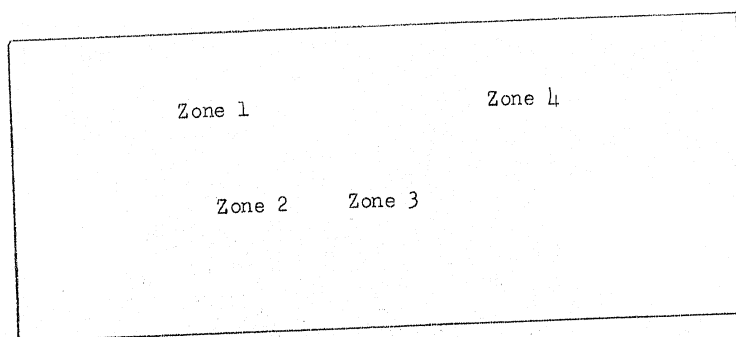
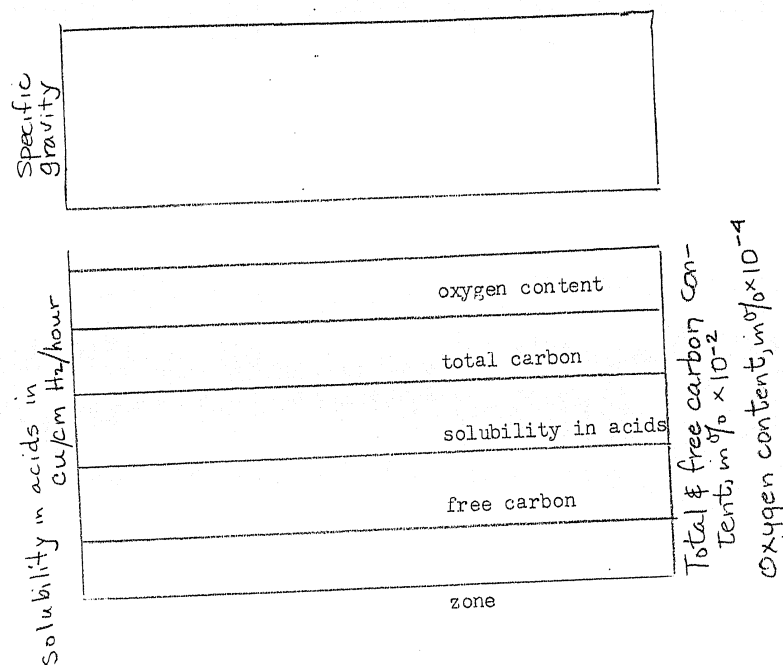


Figure 137. Zonality in carbonyl steel baked with the addition

of 1.2 percent soot (as per Offermann).

The author explains this zonality in the following manner. In the first external zone, which is disposed in conditions of the most ample circulation of atmosphere and the minimum pressure, promoted by the shrinkage in baking, a considerable burning out of carbon took place. Therefore, free carbon is completely absent, while there is comparatively little chemically combined carbon. In the second zone, the circulation of the gaseous atmosphere is somewhat inhibited, in connection with which the burning out of carbon is diminished, and the content of both chemically combined and free carbon is increased. In the third zone, the gas circulation is strongly inhibited, and there is the maximum amount of free carbon. In the fourth zone, the conditions of the gas atmosphere circulation are even worse, but the shrinkage pressure (as a result of baking, the density of the ingot was increased approximately from 3.1 to 5.2 grams per cubic centimeter) is rather considerable, which stimulates contact diffusion. Therefore, this zone, in the presence of the maximum amount of chemically combined carbon, contains very little free carbon.

Thin-walled iron-graphite bush bearings, compressed to 30 percent porosity from a charge of 98 percent iron and 2 percent graphite, and baked at 1100 degrees centigrade, with a time-lag of 40 minutes, in a current of hydrogen, contained

the maximum amount of chemically-combined carbon (about 0.6 percent) in their central parts, and the minimum amount (0.1 percent) in their external and internal edges (see Figure 138, I). In thick-walled bush bearings (Figure 138, II), the maximum amount of chemically-combined carbon (0.6 to 0.7 percent) was to be found in the internal edge, the maximum amount (0.1 percent), in the external edge. Such a disposition of the chemically-combined carbon is due to the fact that, in thin-walled bush bearings, the maximum shrinkage stresses are disposed in a pattern similar to a band (see Figure 138, Ia), while in thick-walled bush bearings, they are disposed in a cylindrical pattern (see Figure 138, IIa).

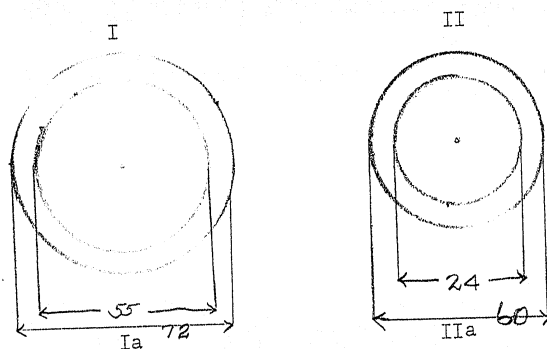


Figure 138. Diagrammatic representation of zonality in the distribution of carburization and stresses in iron-graphite products (the zone of maximum carburization and stress concentration is marked in black).

The briquettes have their maximum density and maximum

contact surface of the particles in their upper part, which is closes to the press plunger. Hence, in a number of cases, the iron-graphite bush bearings have their maximum carbon content in their upper parts.

Figure 139 is a curve graph depicting the growth of carburization of iron-graphite bush bearings in relation to compression density, i.e., in relation to the growth of the contact area between the particles. These results permit the assumption that the carburization of powdered iron is determined by "contact" cementation [case-hardening], and not through the gaseous atmosphere of baking. If cementation were primarily determined by gas reactions, proceeding throughout the volume of the pores, it would be reasonable to expect a diminution of cementation with the reduction in porosity, inasmuch as the accompanying intensity of the burning out of the graphite is lessened.

This is in contradiction to the opinions of most specialists who labored in this field. Thus, according to Minkevich, it has been "unconditionally established that the carburization of iron during the case-hardening process with the aid of carbon proceeds through the gaseous phase". It must, however, be taken into account that, in the case of compact metals, the area of direct contact between the iron and the carbon in the cementation box, constitutes only less than 0.0001 of the total surface of the iron articles. While in the case of compressed and baked iron-graphite powders, the contact surface

between the iron and the graphite attains the value of 0.1 of total surface of the metal. Hence, the phenomena of contact cementation [case-hardening] are of considerable importance in the case of metal powders.

XC

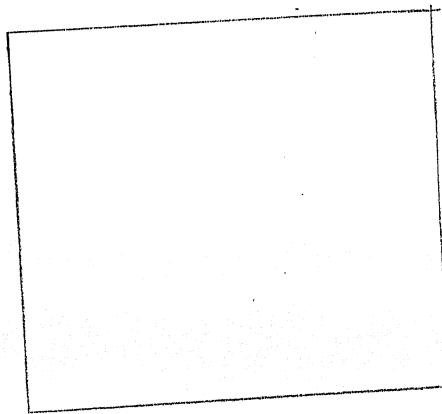


Figure 139. Ratio between the content of chemically-combined carbon and the porosity of iron-graphite briquettes (baking for 1 hour at 1100 degrees centigrade, initial graphite content of 2.5 percent).

84. The Baking of Multiple-Component Mixtures with the Formation of a Liquid Phase

We have seen before that, in baking, a solid single-component metal behaves in a manner similar to a two-phase system. One phase is constituted by the less mobile atoms of the internal layers of particles. The second, sort of "liquid phase", is formed by the surface boundary layer of the most mobile

atoms. We have also noted that the processes of baking and recrystallization are processes of the exchange of atoms and the exchange of mobilities between the sort of a solid and low-mobility "phase" and the sort of a liquid and higher-mobility "phase".

Thusm the baking of a solid homogenous metal powder, at a temperature lower than the melting point of the metal, constitutes a sort of an ultimate case of the baking of a two-phase system at a temperature above the melting point of the more easily-fusible phase (under the condition of the solubility of the solid phase in the liquid phase).

For the attainment of full contact between the particles and full compactness of the material, this ultimate case cannot favorably be applied. First of all, the "liquid phase" is so negligible, by the amount of substance entering into it, that serious doubts are evolved as to whether it can be at all called a "phase". In addition, the number of "liquid", or higher-mobility atoms is greatly reduced during the process of baking. Therefore, the rate of creep and, consequently, the rates of shrinkage and particle growth during the baking in solid state are negligible. Secondly, the fluidity of this "liquid phase" is relatively small (or, which is the same, its viscosity is relatively great). Hence, such a "liquid phase" fills the difficultly-accessible capillary pores very slowly and not completely (see Paragraph 71), particularly when the

baking is done not in vacuum. Thirdly, in the last stages of baking, the process of particle growth is more rapid than the process of shrinkage, and the internal closed pores, being included in the grains, their further filling becomes exceptionally difficult. Fourthly the initial area of the contact sections between the particles is small. It is impossible to obtain a non-porous structure at the expense of a denser cold-pressing, since with the growth in the density of the briquettes, the residual stresses are increased. As a result of this, with the growth of density in the briquettes, shrinkages are reduced, and there begins a growth which increases the initial porosity.

These disadvantages are eliminated to a considerable extent when baking a mixture of powder consisting of two or several components, it being the case that a certain lesser part, which becomes liquefied, dissolves a part of the solid material. This case, in its turn, can be subdivided into two:

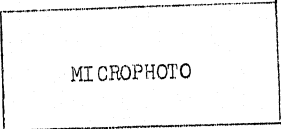
(1). The solubility of the liquid phase in the solid phase is relatively low, hence, regardless of the time-lag at the given temperature, the system remains heterogeneous.

(2). The solubility of the liquid phase in the solid phase at the temperature of baking is so negligible that, after a certain time, the system becomes homogeneous.

Let us analyze the first variant. Let us bake a powder mixture of two metals -- a more refractory basic component A and a less refractory so-called cementation component B, at a temperature above the melting point of the solution of A in B. For purposes of simplification, let us assume that the cementation component B is completely non-soluble in A at the baking temperature, although, as properly indicated by Jones, nothing will change in principle, if there is some solubility of B in A (provided, the heterogeneity of the structure is preserved). The inevitable consequence of the solubility of A in B is the exchange of atoms between the solid and the liquid phase, even after the formation of a saturated solution. In the saturated solution, there exists a dynamic equilibrium between the atoms dissolving in the solution and the atoms escaping from the solution. It being the case that, first of all (see Paragraph 53), the maximum-mobility atoms are dissolved, and the minimum-mobility atoms are liberated. Therefore, the dissolving atoms are predominantly the atoms in the ribs and in the angles of the particles, while at the places of contact, where the atoms have minimum mobility, there is the liberation of the atoms A from the solution. Thus, there is continuous constriction of atoms A through the liquid phase to the contact places of the particles, accompanied by intensive baking shrinkage. Parallel with the process of shrinkage, there is also the growth of the grain, since in the fine particles the number of mobile atoms is greater than in the coarse particles. Therefore, in

the case of fine particles, the number of atoms dissolving per unit of time is greater, and the number of atoms liberated from the solution per unit of time is smaller than in the case of coarse particles. Hence, there is continuous growth of coarse particles at the expense of fine particles (Footnote). The explanation of the mechanics of the grain growth as the result of the differences in solubility, has been borrowed from the thesis by Price, Smithells, and Williams (128). However, they failed to explain the mechanics of shrinkage and of the growth of the contact surface at the expense of these differences). It being the case that a very large grain growth in the basic component A occurs even at very low temperatures, sometimes less than 40 percent of the absolute melting point. The shape of the crystallites in such recrystallization, which can be qualified as recrystallization through the liquid phase, is the same as in the initial crystallization from the metallurgical smelt of the primary crystals of cast alloys. Bochvar (15) notes two basic shapes of the primary crystals of cast alloys -- faceted (Figure 140a, primary crystals of Sb in the Sb-Pb alloy) and oval (Figure 141, primary crystals of Ag in the Ag-Cu alloy). According to Bochvar, the various shapes are due to the differences in the surface tension of the compact metals, which, in the rounded crystals is relatively great, in the faceted crystals -- relatively negligible. In powder alloys, baked in the presence of a liquid phase, the same two shapes of grains of the basic component are observed (and probably due to the same causes).

Figure 141a is a microphoto of the faceted crystallites WC in hard alloys (WC - TiC - Co). Figure 141b shows the oval grains of iron in the iron-copper powder alloys.



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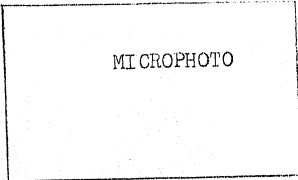
Figures 140a and 140b

Figures 140a and 140b (Text, page 293).

a. faceted primary crystallites Sb in the Sb-Pb cast alloy; b. oval primary crystallites Ag in the Ag-Cu cast alloy (as per Bochvar).



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Figure 141. Faceted crystallites WC in a baked alloy -- 86 percent WC, 5 percent TiC, 9 percent Co X 1000 times (as per Kieffer and Hotop); b. oval crystallites Fe in the

baked alloy Fe-Cu X 500 times (as per Price, Smithells, and Williams).

In toto, shrinkage, the growth of the contact surface of the particles, and the growth of the grain in baking, in the presence of a liquid phase, amount to the similar growth of the number of the less mobile atoms at the expense of the more mobile atoms, as in the baking of pure metals. However, in baking with the formation of a liquid phase greater contact between the particles, practically theoretical density, and greater strength, can all be attained, as due to the following:

(1). The number of the mobile atoms in the basic component is considerably greater than in the case of the baking of pure metals. In pure metals, the number of the higher-mobility (surface) atoms, at its maximum, attains a value of 1 percent (Table 43 in Paragraph 53), and through the process of baking becomes rapidly diminished to negligible fractions of a percent. However, in baking with the formation of a liquid phase, the number of the higher-mobility atoms (surface and dissolved) constitutes several percent and is diminished at a much slower rate with the time lag. Therefore, the rate of creep (shrinkage) is greatly increased in baking.

(2). The fluidity of the liquid phase (and consequently, the mobility of the dissolved atoms) is much greater than the fluidity of the surface semi-liquid layer of pure metal (consequently, than the mobility of the respective atoms). Hence,

the difficultly-accessible capillary pores are easily and rapidly filled.

(3). The area of initial contact between the particles of a mixture is greatly increased at the expense of the liquid phase spilling over the surface (contact through the liquid phase).

(4). Shrinkages are increased with the increase in "effective" porosity. Hence, in an alloy with a porosity of 30 percent and a liquid phase of 20 percent-volumetrically, the volume of the solid phase is the same as in a solid metal with a 50 percent-porosity (see Paragraph 75).

(5). The filling of the large interparticle pores is facilitated by the "centrifuging" of the liquid phase into these pores during the shrinkage.

(6). During the growth of the grain, there is no such affinity to the formation of difficultly-filling intraparticle pores, as baking without the formation of a liquid phase, since recrystallization takes place through the cementation phase, and not through direct contact. This specifically is the circumstance that facilitates the attaining of practically theoretical density in baking.

(7). Permeability (see Paragraphs 12, 40, and 71) in powder alloys baked in the presence of a liquid phase, is much greater than in powder metals baked in the absence of

a liquid phase (at the same degree of porosity). This is due to the greater smoothening of the profile of the particles, and also to the possibility of the translocation of the liquid phase from some pores into other pores. Enhanced permeability facilitates the filling of the capillary pores near the contact sections with metal during the process of shrinkage, and is also conducive to the rapid and complete elimination of gases in baking.

The baking with the formation of a liquid cementation phase may be considered as an example of "activated" baking (i.e., baking activated by way of an increase in the mobility of the atoms). Another example of activated baking (at the expense of the oxides) was already pointed out in Paragraph 67.

In cooling, the heterogeneity of the structure is preserved. With diminished solubility, a partial liberation of the basic component from the cementation phase, with the precipitation of this component upon the undissolved grains, becomes possible. This process may lead to the further growth of the grain and, possibly, to increased shrinkage in cooling.

Kieffer and Hotop⁽¹¹⁵⁾ are in error when they assert that, in baking with the formation of a liquid phase, the strength of alloys is determined by the strength of the cementation phase, and that the contact between the particles

of the basic component is effected not directly, but through the cementation phase. They say: "The boundaries between the cementation phase and the undissolved basic metal practically correspond to the boundaries of the grains in cast metal".

Whereas, as per the above outlined opinion of the author, in the process of baking, there must take place the formation of a direct contact between the grains of the basic metal. The empirical proof of the correctness of this thesis lies in the work of Dawihl and Hinnübor⁽⁸⁸⁾. They eliminated from the baked hard alloys (WC - Co) the cementation phase, by dissolving the cobalt in solvents, which did not react upon the basic component -- tungsten carbide. The strength (resistance to bending) of the undissolved carbide skeleton (see Table 56) constitutes, to a certain extent, a gauge of the degree of the direct contact between the grains of the basic component.

[see next page for Table 56]

Thus, at any rate, in the presence of not too high a content of the cementation metal, the contact and the strength are determined, to a considerable degree, directly by the basic component. The reduced strength resulting from dissolving the cobalt is due to the detrimental effect of porosity.

TABLE 56

The Strength of the Carbide Skeleton in Alloys with Various Cobalt
Content (Baking Temperature 1450 Degrees Centigrade, Bak-
ing Time 1 Hour)
(according to Dawidl and Hinnubor)

<u>Cobalt Content, %</u>		<u>Bending strength in kg/sq mm</u>		<u>Volumetric % of the</u> <u>cementation phase</u>
<u>in initial alloy</u>	<u>after dissolution</u>	<u>in initial alloy</u>	<u>in skeleton</u>	
3.0	0.04	126	54	6.1
6.0	0.04	165	45	12
11.0	0.03	185	0	22

However, it is quite probable that the direct contact between the grains of the basic component is rather considerable also in the presence of a high content of the cementation metal. Supposing, out of three grains of carbide, two are linked by direct contact, while the third one is in contact through the cementation phase. In this case, the alloy will disintegrate upon the dissolution of the cobalt, i.e., its strength will equal zero. This, however, is no proof of the absence of direct contact between the carbide grains. In addition, the experiments by Dawihl and Hinnübor have demonstrated that, with the increase in the duration of the baking at 1450 degrees centigrade up to 120 hours, the strength, upon the dissolution of the cobalt, increased to 18 kilograms per square millimeter, i.e., direct contact between the carbide grains was considerable.

The cementation phase is added in the amount of 5 to 30 percent-volumetrically, more frequently 10 to 20 percent. Excessively small amounts of the cementation phase activate the baking to an inadequate degree, excessively large additions will cause liquation, shape distortion, and other defects.

In actual production, these alloys are usually baked at a temperature somewhat above the melting point of the cementation metal (the higher above the melting point, the coarser the initial powders of the basic component).

Examples of this type of alloy are the so-called hard alloys (WC - Co, WC - Ni, WC - TiC - Co), heavy alloys (W - Ni - Cu), iron-copper alloys (Fe - Cu), copper-silver alloys (Cu - Ag), a series of alloys with the admixture of phosphorous on a copper and iron base, and the like. Sometimes, only a negligible degree of solubility of the basic component in the cementation phase is quite adequate for obtaining alloys of this type. For instance, in some cases (2) the author obtained ⁱⁿ copper-lead powder alloys a characteristic growth of the grain through the liquid phase, regardless of the low solubility of copper in lead at the temperature of baking (see Figure 142).

As practical examples of the second version of baking with the formation of a liquid phase, the systems Cu - Sn, Fe - Al - Ni - Co (alnico), and others. In this case, the liquid phase is after a certain time diffused into the basic component, with the formation of a homogeneous solid solution. Thus, the first stage of baking can be considered as a case of baking in the presence of a liquid stage, and the second stage, as a case of baking in the absence of a liquid phase. In this case, too, it is sometimes possible to attain considerable strength and almost theoretical density.

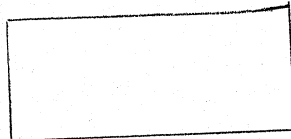


Figure 142. The structure of copper-lead specimens with 25

percent Pb (800 degrees centigrade, 30 minutes) X 500 times, pickled with HNO_3 .

The ratio between the properties of the powder alloys, naked with the formation of the liquid phase, and the various factors, such as the degree of dispersion of the powders, the compression pressure, the temperature, and the time-lag of baking, is basically the same as in the case of pure metal powders.

85. Activated Baking without the Formation of a Liquid Phase

It was pointed out in the preceding text (Paragraphs 82 and 83) that, if in the baking of powder alloys there is no formation of a liquid phase, the baking is usually accompanied by greater difficulties than in the case of pure metal powders. Shrinkages, the growth in strength and in the size of the contact surface, the growth of the particles, all begin, in such cases, at correspondingly higher temperatures. It is basically due to the reduced mobility of the atoms during the formation of solid solutions and compounds.

During the dissolution of the atoms of solid metal in the liquid phase, their mobility, on the contrary, is increased. Here is the basic cause for the activation of the baking process with the addition of the so-called cementation components, fusible at the baking temperature. Shrinkages and strength are increased considerably, the attainment of almost theoretical density becomes possible, the temperature

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of the grain growth and of the attainment of the necessary mechanical properties is reduced considerably.

A very important (in principle) question arises as to whether the addition of some components, non-fusible at the given baking temperature, can perceptibly activate the process of baking. The answer is in the affirmative, if only by analogy with cast alloys.

It was assumed until now that alloys are always less plastic than their initial components, or, at any rate, than one of them. However, Bochvar⁽¹⁹⁾ recently discovered an important phenomenon, which he called hyperplasticity. Certain aluminum-zinc alloys turned out to have at certain higher temperatures greater plasticity than each of the initial components. It is obvious that, in this case, the mobility of the atoms has increased during the formation of the solid solutions. The addition of components, entering into the solid solution, reduces the mobility of the atoms of the basic metal, in the presence of not too high temperatures. But simultaneously it lowers the melting point, i.e., it increases the mobility of the atoms at some predetermined very high temperature, and, probably, also within a certain range below this temperature.

The same phenomena may occur in the baking of powder metals.

Price, Smithells, and Williams, in baking a tungsten

powder at 1400 degrees centigrade, with the addition of about 10 percent of copper and nickel (in the proportion 1:2½), obtained a compact alloy with a sharply pronounced growth of the tungsten grain. They ascribed this effect to the formation of a liquid cementation copper-nickel-phase. By using X - rays, they established that the cementation phase contained in solution 17 percent of W, and the melting point of such a system (see Figure 143) is above 1420 degrees centigrade. Buknal (128), therefore, correctly pointed out the fact that the liquid phase could have been present in the baking process only in the beginning of the latter, with the subsequent solidification of the cementation phase. However, the growth of the grain and recrystallization continued after that. Thus, the presence of the liquid phase is not a prerequisite for activated baking. Moreover, the alloy W - Cu - Ni, baked at 1350 degrees centigrade, i.e. below the melting point of the copper-nickel (1:2½)-alloy, in which no liquid phase could form, still showed considerable growth of the particles and the formation of the characteristic rounded structure (see Figure 144) also considerable shrinkage.

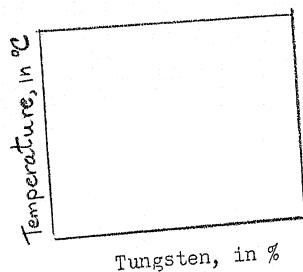


Figure 143. Melting temperatures of alloys W - Cu - Ni (according to Price, Smithells, and Williams)

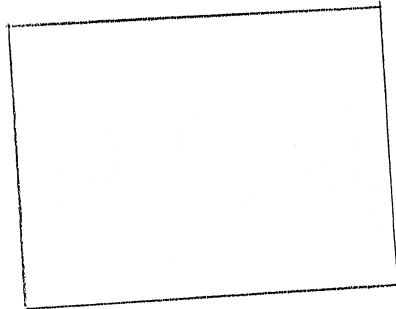


Figure 1111. Microstructure of the alloy W - Cu - Ni baked at 1350 degrees centigrade, X 500 times (in accordance with Price, Smithells, and Williams).

Thus, the liquefaction of the cementation phase is not a prerequisite for activated baking. Seemingly, the cementation phase, even before the melting temperature is reached, is in such a mobile and plastic state, that its entering into the solid solution considerably increases the mobility of the atoms of the refractory component, and activates the baking process. This phenomenon is important not only for its theoretical value, but has great practical value as well, since in baking at temperatures somewhat below the melting point, defects and flaws, linked to the segregation of the liquid phase, buckling, and the like, can be avoided.

CHAPTER XII

HOT - PRESSINGBasic Data

It was pointed out that, as viewed from a scientific angle, pressing can be considered as an increase in the contact between the powder particles at the expense of deformation by external forces, and baking, same as above, except at the expense of the inherent thermal mobility of the atoms. Hot-pressing unites these two operations into one, and, consequently, the growth of contact is attained as a result of the two above mentioned processes. Hence, when hot-pressing is employed, it is easy to attain a 100-percent-density of the final product.

Strictly speaking, hot-pressing should be differentiated from baking under pressure. The difference between these is reduced to the following. The term hot-pressing should be applied primarily to the case when high rates of consolidation and relatively high pressures are employed. In the presence of these, the phenomena of creep manifest themselves relatively little, while diffusion and recrystallization do not proceed to completion. Baking under pressure, on the contrary, is a process of low pressures and low rates of de-

formation. The experimental data available is still inadequate for the creation of a fully developed theory of hot-pressing. The presently known basic regularities of this process can be reduced to the following.

(1). With hot-pressing, it is possible to obtain a final product with a density, approximately the theoretical, and with mechanical properties not below those of cast materials treated under pressure.

(2). With the temperature of hot-pressing, the magnitude of the critical pressure σ_R and of the pressure which is required for the consolidation of the powder to a predetermined degree (see Paragraph 22, Table 24), are diminished. Some exceptions to this ratio may be due to phase transformations or to considerations which were analyzed in Paragraph 22.

(3). At a given pressure, with the rise in pressing temperature, the exponents of strength (tensile strength, compressive strength, bending strength) grow and attain their maximum value at some predetermined temperature. Above this temperature, strength does not change any longer, or, at times, is somewhat decreased. For instance, as can be seen from Table 57 below, compiled in accordance with the data by Henry and Cordiano (101), the tensile strength of iron, compressed under a pressure of 7 kilograms per square millimeter

TABLE 57

The Mechanical Strength of Iron Pressed under Various Temperatures and Time-Lags, the Pressure
Equal to 7 Kilograms per Square Millimeter (as per Henry and Cordiano)

Temperature in °C	Time-lag in seconds	Specific gravity	Tensile strength	Elongation,	Brinell hardness
		in gr/cu cm	in kg/sq mm	in %	
500	[1]	[3]	[4]	[5]	[6]
	50	6.31	18.4	0	50
	150	6.38	22.8	0	51
	450	6.71	28.0	1.0	63
600	50	6.70	25.9	0.5	62
	150	6.89	28.6	1.0	77
	450	7.05	34.2	2.0	80

TABLE 57 (Continued)

[1]	[2]	[3]	[4]	[5]	[6]
	50	7.32	33.5	1.0	90
700	150	7.52	40.1	12.0	95
	450	7.58	40.3	27.0	100
	50	7.59	37.9	22.0	101
780	150	7.71	36.7	32.0	93
	450	7.76	37.0	37.0	96

at 780 degrees centigrade (maintained for 150 and 450 seconds), was somewhat decreased as compared to iron compressed at 700 degrees centigrade.

This ratio is due to the following. Strength depends on three factors: density of the material, the value of the cold-hardening effect, and the content of admixtures and oxides. The increase in density with the rise in temperature is conducive to the growth of strength. However, the residual stresses of the hot-pressing and the content of oxides (when pressing in a reducing atmosphere) are simultaneously diminished, which, on the contrary, diminishes strength. Therefore at some predetermined temperature, there begins a decrease in strength, as promoted by the two above mentioned factors. It follows that the temperature of inflexion is the lower, the greater the content of oxides and the greater the compression pressure. In the presence of a negligible content of oxides and a negligible compression pressure, the point of inflexion may generally be absent.

The presence of the point of inflexion is pronounced with particular sharpness in the hardness-temperature curve, in the presence of great compression pressures (see Figure 145 below).

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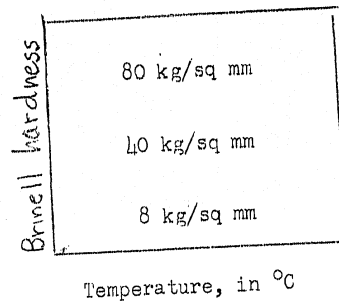
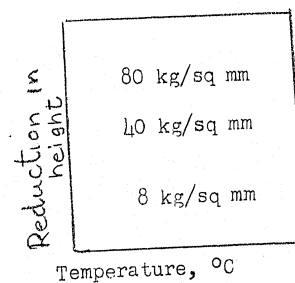
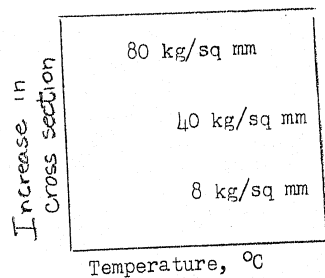


Figure 145. Ratio between the hardness of copper and the compression temperature (as per Goetzel)

The exponents of deformability (elongation, reduction in area, increase in transverse section under compression) continuously increase with the compression temperature (see Figure 146 below), since, in their case, the change in all three above mentioned factors exerts an effect in the direction of improving the mechanical properties.



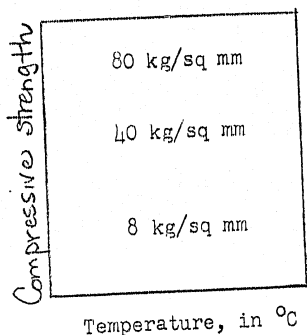


Figure 146. Ratio between the expansion of the cross-section area, the reduction in height, and the compressive strength of copper, on the one hand, and the temperature of hot-pressing, on the other hand (as per Goetzel).

(4). All mechanical properties are improved with the increase in compression pressure, but only up to a certain limit, when 100-percent-density is attained. With the further increase in pressure, the mechanical properties practically remain constant, particularly at higher pressing temperatures. The pressure, at which the constancy of mechanical properties is attained (which in small-height specimens corresponds to the critical pressure) is the lower, the higher the temperature.

(5). The duration of the hot-pressing process is a very important factor, since, at high temperatures, the phenomena of creep play an important part. The more protracted the pressing process, the lower the pressure that is required

for the attainment of specified density and mechanical properties, or, in other words, the greater the density and the mechanical properties, attainable under a predetermined compression pressure (see Table 57). In addition to the phenomena of creep, protracted hot-pressing is linked to a more complete reduction of oxides, recrystallization, and detoughening. All this leads to higher plasticity and, in most cases, to improved mechanical properties, with the duration of pressing (with the exception of hardness and strength at higher temperatures, which may become somewhat diminished through causes indicated in Point 3 above).

(6). The phenomena of recrystallization are observed in hot-pressing. Thus, Goetzel (92) observed visible indications of recrystallization in hot-pressing at a temperature of 500 degrees centigrade (about 60 percent of the melting point). It is characteristic that recrystallization was visibly pronounced in the coarse, and not in the fine, particles. Obviously, this is linked to a smaller content of oxides, and, conformantly, to a more rapid reduction in the coarse particles at a relatively short duration of the hot-pressing operation.

(7). The annealing of hot briquettes is connected with further recrystallization, leveling of the structure, and changes in density. According to Goetzel (92), some shrinkage is manifested in low-density briquettes, while

a growth of dimensions is manifested in briquettes of high density. The phenomena of shrinkage and growth of dimensions in hot briquettes are due to the same causes as in the case of cold briquettes. For instance, the growth in dimensions can be explained by the liberation of gases during the prereduction of oxides, by the absorption of residual stresses, and by zonal isolation.

CHAPTER XIII

THE PROPERTIES OF BAKED POWDER METALS

87. The Properties of Porous Metals

Cohesion in baked porous metals, in contradistinction to baked powder briquettes, is basically determined by molecular cohesion, and not by engagement between the grains. At the same time, as in the case of briquettes, the smallest and the weakest cross section is the "contact" cross section (see Paragraph 16), which passes completely through the contact boundaries of the grains and through the pores. Very frequently during the disintegration of baked porous metals, a fracture follows the same line as in the case of briquettes, between the grains, and not through the grains, as in the case of most compact metals.

But in contradistinction to briquettes, the "contact" cross section in baked porous metals is not always held to minimum dimensions. For instance, if the pores, as a result of baking, were transformed from intercrystalline into intracrystalline, the contact cross section is already not at its minimum value. If total porosity is negligible, the contact cross section, even when the pores^{are} of the open type, will not always be at its minimum value, since shrinkage in baking

first of all reduces the volume of the pores closest to the places of contact. The contact surface of the grains has an uneven outline, and does not always pass perpendicular to the deformation stresses. Deformation by way of intracrystalline sliding in plastic metals, as is known, requires smaller stresses than disintegration along the boundaries of the grains, tied in with each other, as is the case in baked porous metals (in contradistinction to briquettes), by the forces of cohesion. Therefore, the "contact" cross section of baked metals, even though it may be of minimum dimensions, must not necessarily be of minimum strength. This is the reason why, in a number of cases, a fracture in plastic metals with low porosities passes not along the contact cross section, but through the pores.

Thus, baked porous metals, by their mechanical properties, constitute a sort of transition step between powder briquettes and compact metals. The greater the plasticity and the smaller the porosity of the baked metal, the closer it approximates, in its mechanical properties, the compact metal. The greater the brittleness and porosity of the baked metal, the closer are its mechanical properties to those of briquettes.

In the presence of elastic deformation, the size of the contact cross section remains practically constant. Hence, the properties of baked porous metals, which depend on elastic de-

formation, are linked to the size of the contact cross section and to the mechanical properties of compact metals in a rather simple manner. For instance, the yield points in tension and in compression for baked porous metals are to the corresponding yield points for compact metals (approximately) as the size of the contact cross section A'_H is to the nominal size of the transverse section of the specimen A:

$$\frac{\sigma_s}{\sigma_{sk}} = \frac{A'_H}{A} = \alpha \quad (87/1)$$

where σ_s is the yield point in tension for the porous metal;

σ_{sk} is the yield point of the compact metal;

α is the ratio of the area of the contact cross section to the nominal area of the transverse section.

It follows from formula (87/1) that the true yield point for the porous metal, i.e., the stress, as related to the contact cross section $\frac{\sigma_s}{\alpha}$, is equal to the yield point of the corresponding compact metal. Usually, the yield points of porous metals in compression are somewhat higher than they are in tension (see Table 58). But in the case of very porous or very brittle and hard baked metals, the yield point in compression may at times, as also in the case of briquettes, be considerably greater than the yield point in tension. The moduli of elasticity for baked porous metals, in the presence

of a negligible contact cross section value, are rather close to the moduli of elasticity for briquettes. If the size of the contact cross section is increased in baking, the modulus for the baked metal is greater than for the initial briquette. If the size of the contact cross section is diminished in baking, then, on the contrary, the modulus for the baked metal may even be diminished. In the presence of a considerable contact cross section, the value of the moduli of elasticity for the baked metals approaches the corresponding values for cast metals.

In the presence of plastic (or generally non-reversible) deformation, the size of the contact cross section changes. Therefore, the ratio between the mechanical properties of porous metals, which are determinable by the non-reversible deformation and the contact section, and also between the corresponding properties of compact metals, is more complex than in the presence of elastic deformation.

In the presence of tension beyond the yield point, there occurs a non-reversible diminution of the contact cross section. It may be expressed by way of a breakoff of the contact surfaces (particularly in the presence of high porosity and in the case of brittle metals), as well as by way of the result of plastic deformation (particularly in the presence of a considerable initial size of the contact cross section). The true ultimate tensile strength of a porous

metal, computed for the actual size of the contact surface at the moment of the break, is possibly above the true yield point of the porous metal (but possibly below the true ultimate strength of the compact metal). However, in connection with the rapid breakoff of the contact surfaces, the nominal ultimate strength σ_b for metals of considerable porosity, as related to the nominal transverse section, is almost equal to its nominal yield point σ_s (see Table 58). It is possible that, in tension, at the moment preceding the break, a certain diminution of the corresponding contact cross section and an elongation of the breaking grains takes place. However, in the presence of considerable porosity, these changes will not manifest themselves upon the nominal dimensions of the specimen. Therefore, in the case of metals of high porosity, elongation and reduction in area are practically equal to zero. By the same token, impact ductility, too, in porous metals, is insignificant. With a diminution of porosity, an intercrystalline fracture is transformed into an intracrystalline one, the ratio $\frac{\sigma_b}{\sigma_s}$, elongation, and reduction in area are all increased, approaching, in their ultimate values, the corresponding values for compact metals.

Under compression, in contradistinction to tension, the contact cross section, on the contrary, is increased. Therefore, the ratio of the ultimate compressive strength to the yield point is, in this case, not less, but considerably greater than for the corresponding compact metals. Porous

metals are very "brittle" in tension. In compression, on the contrary, porous metals are characterized by exceptionally high deformability (under much lower pressures than is the case in cast metals, since their yield point is considerably lower). This high deformability is very important in two respects:

- (1) as a result of it, porous metals have greater machinability under pressure than cast metals;
- (2) porous parts, operating in friction, due to their high deformability, have exceptionally good run-in qualities and considerable resistance to wear.

The ratio between deformation and load, in the case of baked porous metals, as well as in the case of non-baked powders, is expressed by the differential equation (19/2)

$$\frac{dp}{A'_H} = \pm k dh,$$

where

p is the load;

A'_H is the size of the contact cross section;

k is a constant coefficient;

h is the height (length) of the final product;

the plus sign pertains to tension, the minus sign pertains to compression.

In the baked product, the ratio between the contact cross section and the load is expressed not by formula (16/1), but by the following equality:

$$A'_H = A_0 + \frac{P - P_0}{\sigma_R} \quad (87/2)$$

where A_0 is the initial size of the contact cross section (prior to the application of the load);

P is the load;

P_0 is the ultimate value of the load, prior to the attaining of which A_0 practically does not change (the elastic deformation of the contact);

σ_R is the critical stress (contact strength) of the metal. Formula (87/2) is true only for the case where $P > P_0$.

The ratio between A_0 and P_0 may be expressed in approximation by formula

$$A_0 = \frac{P_0}{\sigma_R} \quad (87/3)$$

where:

$$A'_H = \frac{P_0}{\sigma_R} + \frac{P - P_0}{\sigma_R} = \frac{P}{\sigma_R} \quad (87/4)$$

Thus, for the case when $P > P_0$ the following formula can be written down:

$$\frac{dP}{P} = \pm \frac{k}{\sigma_R} dh. \quad (87/5)$$

It follows from this that, in the compressive reduction of a baked metal in a calibration press mold, the ratio between the pressure p and the relative volume β will be expressed, as in the case of non-baked powders, by formula (when $p > p_0$):

$$\log p = \log p_k - L(\beta - 1), \quad (87/6)$$

where p_k is the pressure corresponding to the consolidation to a compact state (in the case of a net pressure equal to σ_R).

Indeed, from the calibration diagram for baked copper (initial porosity 43 percent), shown in Paragraph 21 (Figure 43, b), it follows that for calibration pressures within the range 10 - 30 kilograms per square millimeter, the σ_R -value attained was 78 kilograms per square millimeter (the hardness of toughened copper).

In connection with the different characteristics in the change of the contact cross section in the case of porous metals, correlations between the mechanical properties in tension and in compression, which are unusual in the case of compact metals, are observed in the case of porous metals (see Table 58 below).

TABLE 58

The Mechanical Properties of Baked Porous Iron (Porosity 25 Percent)

<u>Mechanical properties</u>	<u>Fine powder</u>	<u>Medium powder</u>	<u>Coarse powder</u>
Tensile strength, in kg/sq mm	8 - 11	4 - 10	up to 4
Yield point in tension, kg/sq mm	8 - 10	--	--
Bending strength, kg/sq mm	15 - 25	8 - 16	up to 8
Compressive strength, kg/sq mm	50 - 70	40 - 60	30 - 45
Yield point in compression, kg/sq mm	up to 12	--	--
Elongation in tension, in %	0 - 1	0	0
Shrinkage in compression, in %	about 50	about 40	about 30
Impact ductility, in kg-cm/sq cm	12 - 40	8 - 12	up to 8
Brinell hardness, in kg/sq mm	40 - 60	30 - 45	up to 35

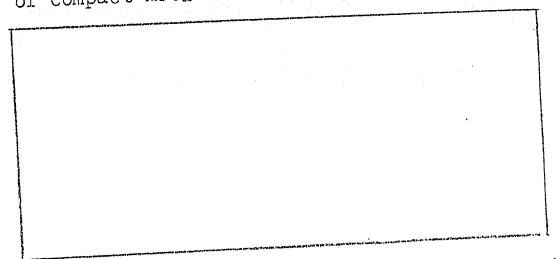
Let us point out additionally some of the features of the ratio between the mechanical properties of porous metals and their porosity and composition.

(1). The mechanical (and other) properties of a porous metal are determined not by porosity directly, but by the size of the contact cross section. In the presence of the same degree of porosity, the magnitude of the contact cross section may oscillate considerably in relation to the physical characteristics of the initial powders, their chemical composition, conditions of pressing, baking, and the further treatment of the products, the correlations between the intra- and inter-crystallite porosity, and the like. Therefore, the properties of metals with the same degree of porosity may differ in various manners from the properties of the corresponding compact materials.

(2). The study of the phenomena of pressing revealed that the contact cross section grows at a much higher rate than with the first power of density. This also pertains, to a certain extent, to baked products. Therefore, mechanical properties usually increase more rapidly than with the first power of density, and the curves density (porosity) -- mechanical properties, have, in most cases, their convexities downward (see Figure 147). However, the ratio between the contact cross section and porosity in baked metal is considerably more complex than in briquettes. For instance,

intracrystalline porosity reduces the mechanical properties to a considerably lesser degree than intercrystallite porosity. Therefore, in some cases, the mechanical properties, with the diminution of porosity may grow in a different manner than what is shown in Figure 147, a, namely in accordance with Figures 147, b and 147, c. Figure 148 depicts the ratio between a number of mechanical properties, on the one hand, and porosity, on the other hand, in accordance with Lenel (121), and Figure 149 depicts the same as above, in accordance with Bal'shin and Korolenko (3).

Mechanical properties
of compact metal



0 Relative density → 100 percent

Figure 147. Diagram of the ratio between the mechanical properties of baked metals and porosity.

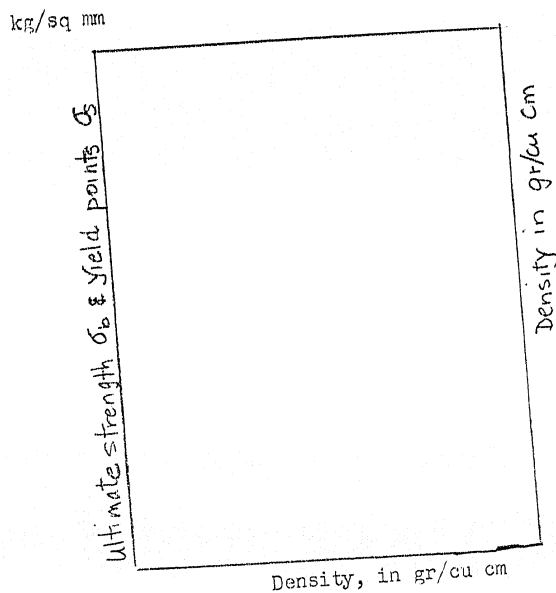


Figure 148. Ratio between the mechanical properties of iron and porosity (according to Lenel).

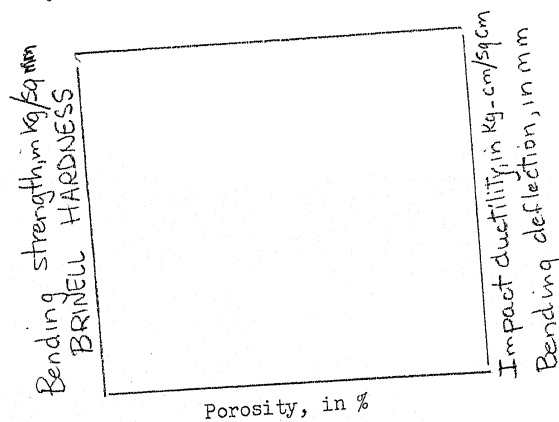


Figure 149. Ratio between the mechanical properties of iron,

with a 2 percent admixture of graphite, and porosity
(in accordance with Bal'shin and Korolenko):

1. Brinell hardness;
2. bending force;
3. impact ductility;
4. bending deflection.

(3). The contact cross section of briquettes, with the diminution of porosity by 1 percent, grows by 2 to 10 percent, most frequently by 3 to 5 percent. The mechanical properties of baked materials change approximately in the same manner, i.e., with the change of porosity by 1 percent, they change by 2 to 10 percent, in most cases, by 3 to 5 percent.

(4). With the same degree of porosity, materials baked from coarse powders, usually have a smaller contact cross section, a greater number of interparticle pores, and larger pores than materials obtained from fine powders. Therefore, the mechanical properties of articles made from coarse powders (see Table 58), in the presence of the same degree of porosity, usually are of lower values and increase, with the diminution of porosity more rapidly, as compared with the properties of briquettes. There are some exceptions to this rule, when materials, made from fine powders, on the contrary, have mechanical properties of a lower value. Most

frequently, these exceptions to the rule are due to an increased content of oxides.

(5). In the presence of the same porosity, harder and more brittle materials have a smaller contact cross section than softer and more plastic materials. Therefore, not to mention the indexes of deformability, the strength of hard porous metals constitutes a smaller part of the strength of compact material than the strength of soft materials of the same porosity. In connection with this, the mechanical properties of porous metals of various chemical composition differ to a smaller degree than in the case of the corresponding compact metals. At times, there is even an inverted ratio, by comparison with compact metals. For instance, with the same degree of porosity, porous steel may have a lower strength value than porous iron, and porous iron may have a lower strength value than porous copper (compare with the properties of briquettes). It is also to be noted that the properties of hard metals, with a diminution of porosity, grow more rapidly than the properties of soft metals.

(6). Porous alloys, baked with the formation of a liquid cementation phase, have a higher degree of contact between the grains, a greater number of intercrystallite pores, and relatively higher mechanical properties, as compared to other metals and alloys having the same porosity.

(7). Porous alloys, containing components, the oxides of which are difficultly-reducible, or components which decrease weldability, baked without the formation of a liquid phase, have low mechanical properties (for instance, siliceous cast irons with a silicon content of over 5 percent).

(8). Usually, the mechanical properties of porous alloys are the lower, the greater the number of components in their composition (see Paragraph 82), particularly when baked without the formation of a liquid phase.

(9). The machining of porous metals by cutting reduces their mechanical properties. This reduction in the mechanical properties is the more sharply pronounced, the greater the porosity and the brittleness of the metal. Hence, specimens that are designated for mechanical testing must not be machined by cutting.

88. The Properties of Consolidated Baked Metals and Alloys

In most cases, metalloceramic metals and alloys, developed by corresponding post-baking treatment to full compactness, have the same mechanical and physico-chemical properties as compact cast metals of the same composition after pressure treatment (see Tables 59 and 60 below).

This does not in any way support the assumption by Jones ⁽²⁷⁾ that the boundaries between the grains of a metal, obtained by the method of powder metallurgy, are of a differ-

ent nature, as compared to the boundaries between the grains of a metal obtained by the conventional methods of casting.

Certain properties of consolidated metalloceramic materials, due to various reasons, are at times higher than in metals obtained by pressure-casting [die-casting] methods. Thus, Offermann (126) notes that metalloceramic carbonyl steels, due to a lower content of silicon, manganese, phosphorous, and sulfur, have greater weldability than conventional steels. It follows from Table 59 that the electrical conductivity of consolidated metalloceramic copper is higher than that of conventional electrolytic copper, which is due to the lower oxygen content. According to Kelly, metalloceramic beryllium has higher mechanical properties than cast beryllium, due to the greater fineness of its granular structure.

It is possible that the properties of some consolidated metalloceramic materials may be lower than those of cast materials. Thus, it may be assumed (though it was never checked) that in metalloceramic materials with a high content of components, which form difficultly-reducible oxides or decrease weldability (for example, cast iron containing 3 percent silicon), the properties should be of a lower value than in the corresponding cast materials.

TABLE 59

Properties of Copper in Relation to the Method of Obtaining (in Accordance
with Goetzel⁽⁹²⁾ and Kieffer and Hotop⁽¹¹⁵⁾)

Method of obtaining	H_B in kg/sq mm	σ_b in kg/sq mm	δ in %	γ in gr/cu cm	λ m/ohm-sq mm
	[1]	[2]	[3]	[4]	[5]
Casting	40 - 50	15 - 20	15 - 25	8.9	55 - 57
Casting after forging, rolling and annealing	>50	20 - 24	>38	8.93	57 - 59
Casting after an 80% rolling deduction	100 - 110	44	10 - 12	8.93	55 - 57
Cold-pressing under 6 t/sq cm, baking at 600° C	45	14 - 16	3 - 4	7.6	32 - 36

Table 59 (Continued)

<u>Method of obtaining</u>	[1]	[2]	[3]	[4]	[5]
Hot-pressing under 6 t/sq cm at 300°C	100 - 110	25 - 30	--	8.9	--
Same, except under 15 t/sq cm, at 400°C	120 - 150	30 - 35	--	8.9	57 - 59
Cold-pressing under 3 t/sq cm, baking at 90° C, hot deformation 90%, annealing	40 - 50	20 - 25	35	8.9 - 8.93	59 - 62
Same as above, after a 50% hot-rolling reduction and cold deformation	100 - 110	35 - 40	10 - 12	8.9 - 8.93	55 - 57

TABLE 60

Properties of Iron in Relation to the Method of Obtaining (in accordance
with Goetzel (92) and Kieffer and Hotop (115))

Method of obtaining (or state)	Relative density in %	H_B	Yield point in in kg/sq mm	σ_b in kg/sq mm	Reduction	
					δ in %	in area in %
[1]	[2]	[3]	[4]	[5]	[6]	[7]
1. Cold-pressing (8 t/sq cm)	77 - 83	70 - 75	--	0.28 - 0.35	--	--
2. Pressing (6 - 8 t/sq cm), baking at 1000°C	83 - 88	40 - 50	--	17.5 - 21.0	8 - 12	8 - 12
3. Same as above, but re-pressed under 6 - 8t/sq cm	90 - 93	65 - 70	--	23 - 29	0 - 3	0 - 3
4. Same as (3), but re- baked at 1000°C	90 - 93	55 - 65	11 - 14	23 - 26	16 - 22	16 - 22

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	[1]	[2]	[3]	[4]	[5]	[6]	[7]
5. Hot-pressing at 810°C (3.5 t/sq cm)	95 - 100	60 - 100	--	35 - 40	--	--	
6. Same as (2), but followed by hot- forging	100	90	21	35.5	35	60	
7. Electrolytic iron, resmelted, rolled, and annealed	100	45 - 90	7 - 14	24.5 - 28	40 - 60	70 - 90	

In the case of compact metalloceramic alloys obtained by baking, with the formation of a liquid cementation phase, without subsequent pressure-treatment, the properties are not only not lower, but usually even higher than in the corresponding cast alloys. Thus, in accordance with the data by Kieffer and Hotop⁽¹¹⁵⁾, the strength of the metalloceramic hard alloys WC - Co is 5-6 times higher than the strength of the cast alloys. This is primarily due to the fact that in the cast alloys the tungsten carbide WC is disintegrated into W₂C and graphite. By the same token, the mechanical properties of the baked magnetic alloys of the alni (Fe - Al - Ni) and the alnico (Fe - Al - Ni - Co) type are somewhat higher than in the cast alloys⁽¹¹⁵⁾, due to the fine granularity of the metalloceramic materials.

A special type of compact metalloceramic alloys are compositions consisting of components, which do not form any solutions and chemical compounds in a liquid or in a solid state, as for instance, copper-graphite brushes and copper-tungsten contacts. Such compositions are used in the electrical industries on account of the additivity of their properties. For example, the composition of copper-tungsten combines the hardness, the strength, and the refractoriness of tungsten with the high electrical conductivity of copper. In contradistinction to solid solutions and compounds, the electrical conductivity of the composition is not reduced, but is an additive of the same in the initial components.

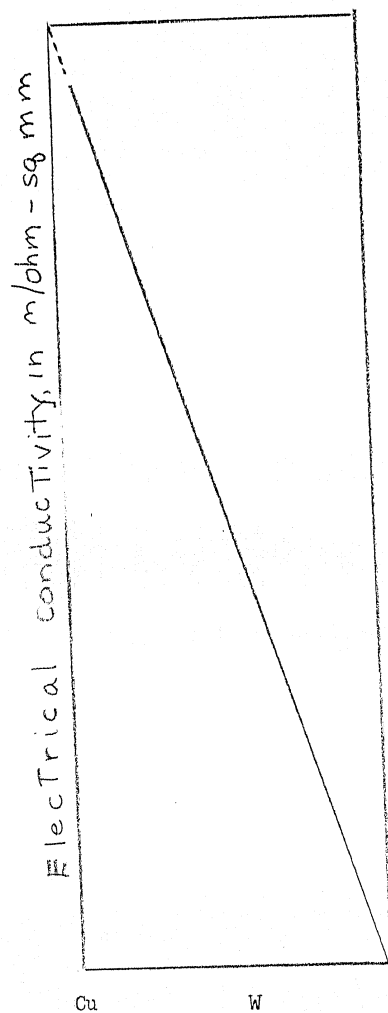


Figure 150. Electrical conductivity of W - Cu alloy in relation to the variation in its composition (as per Kieffer and Hotop).

CHAPTER XIV

THE IMPORTANCE OF POWDER METALLOGRAPHY

General Notes

The development of powder metallography, as well as any other new branch of science, passes through three consecutive stages.

(1). The first stage is characterized by drawing upon the experience of adjacent disciplines and by development of the fundamentals of powder metallography, which the latter has in common with other branches of science.

(2). The second stage is characterized by the development of the specific fundamentals of powder metallography, by which it is differentiated from other branches of science.

(3). The third stage is characterized by the utilization of the experience accumulated by drawing upon the adjacent disciplines.

Powder metallography is of great importance to those branches of science which are occupied with the study of substances with incomplete contact between their structural elements, such as ceramics, the science of the soil, the theory of free-flowing substances, etc. Over 10 years ago, the reknown specialist in the field of ceramic production,

Ryzhkevich, remarked that, regardless of the tender age of powder metallurgy, its scientific fundamentals, in a number of cases, are already developed to a greater extent than in the field of ceramics. The experience of powder metallography may also be utilized in all the branches of science dealing with contact between solid bodies, such as the theory of friction, the theory of cutting, the theory of catalysis, and various subdivisions of physical chemistry, and others.

Within the framework of this book, the author, however, is confined to a rather brief and incomplete discussion on the subject of the specific importance of powder metallography in the general field of metallography.

90. Powder Metallography and the Study of Deformation and Strength

Powder metallography creates the possibility (and at times even compels) to contemplate many conventional concepts and phenomena from unusual angles. Hence, the knowledge of powder metallography, if only for this reason, assumes a certain value for the better understanding of even the most elementary phenomena in the deformation of metals. It is particularly useful in the understanding of contact phenomena, which are of great importance when dealing with problems of deformation and strength in metals.

Not only engineers, but even laymen without any education at all are familiar with the concept of hardness in materials. But hardly even all the experts in the testing of metals clearly

understand that hardness in essence is nothing else but the contact strength of the material, and that hardness, in terms of Brinell, Vickers, or Meyer units, is the stress which is required for the formation of a unit of contact surface in the presence of the corresponding methods of testing. It is common knowledge that the harder material will always deform scratch, or cut the softer material, and not the other way around. But there will hardly be found many experts in the field of the testing of metals who would know that this phenomenon is due to the fact that the stress at the place of osculation of materials of different hardness is always equal to the contact strength (hardness) of the softer material, and is always less than the contact strength (hardness) of the harder material. The study of powder metallography makes it possible to develop a clear concept of hardness as the contact strength of the material.

A new contact surface (planes of sliding) is formed during plastic deformation, and a new free surface is formed during brittle deformation. Thus, any non-reversible deformation is closely tied in with the formation and destruction of a contact surface.

Powder metallography somewhat expands our range of vision in the study of the cold-hardening of metals. Compression diagrams for powders (see Paragraph 22) indicate an unusual ratio between toughening at the moment of deformation,

on the one hand, and the metal of the powder and the temperature of pressing, on the other hand. Toughening is greater in the pressing of soft metal powders (including such as tin and lead) and in the presence of higher pressing temperatures. Hardness and strength measurements of cast compact metals following deformation (when, in the case of soft metals, the phenomena of detoughening are of considerable importance) show a reversed ratio between cold-hardening and temperature and hardness of the metal. However, on the other hand, measurements of the true strength of compact metals (as related to the actual cross section area at the moment of deformation or disintegration) permit the deduction that in compact metals, at the moment of deformation (but not after it), in a number of cases, the same ratio between cold-hardening and the type of metal and temperature exists as in the case of powder metals. The true strength of a metal essentially is determined by the degree of toughening, which it can sustain without disintegrating, in the presence of a given type of deformation. For instance, the ratio between the true tensile strength of a compact metal and its yield point in tension characterizes the maximum degree of cold-hardening which the metal can sustain without disruption in tension. In the case of hard metals, such as compact tungsten, this ratio is somewhat greater than unity. For metals of medium hardness, such as iron, it attains a value of 5 to 6, and for softer copper, its value is still higher. Thus, the maximum degree of cold-hardening, in the presence of tensile deformation, increases with the drop in the hardness of the compact metal being tested. A similar

ratio occurs in the compact metal in the presence of other types of deformation. For instance, the concept of cold-hardening, in the presence of contact deformation, can furnish the ratio between hardness (contact strength) and the yield point of the metal in compression. This ratio is approximately 3 to 4 for tungsten, 5 to 6 for iron, and above that for copper, i.e., the degree of cold-hardening in compact metals can be increased with a reduction in hardness, also in the presence of contact deformation. According to Shevandin (69), the yield point σ_s increases $3\frac{1}{2}$ times, and the ultimate strength

σ_b only two times, if the temperature is reduced from room temperature to minus 196 degrees centigrade. In other words, the ratio $\frac{\sigma_b}{\sigma_s}$, which is characteristic of the degree of cold-hardening in the presence of deformation, with the reduction in temperature, is decreased 1.75 times. Kostenets and Ivanchenko (34) cite similar data -- in the case of 1010-soft steel, at room temperature the ratio $\frac{\sigma_b}{\sigma_s} = \frac{37}{23} = 1.61$; reduction in area $\psi = 75$ percent. At minus 196 degrees centigrade, $\frac{\sigma_b}{\sigma_s} = \frac{73}{72} = 1.01$, and $\psi = 4$ percent. In deoxidized copper (99.97 percent Cu), in accordance with the Manual of the Bureau of Standards (152), the ratio between the ultimate tensile strength to the proportional limit, at 205 degrees centigrade equals $\frac{25.8}{8.8} = 2.82$, and at 30 degrees centigrade it equals $\frac{30.3}{12.9} = 2.35$. These examples show that in cast metals the degree of cold-hardening in the presence of deformation becomes increased with the rise in

temperature. Thus, by a more careful study, it is possible to discover in compact metals, in a number of cases, an analogy with the unusual behavior of powder metals in the presence of cold-hardening.

The mechanical properties of briquettes appear to be completely unusual. The hardness (the contact strength) of briquettes (compressed under the same conditions) increases not with the increase, but with the decrease in the hardness of the metal of the initial powder (see Paragraph 50). The compressive strength of powder briquettes also increases with a decrease in the strength of the metal of the initial powder (see Paragraph 45). Such an unusual ratio is observed less frequently in baked porous metals. However, as a rule, the difference in strength between different metals (having the same porosity) is less sharply pronounced than between the corresponding compact metals. Thus, also after the baking of the briquettes, the smaller strength of the softer and more plastic initial metal of the powder is as if compensated by its greater capacity for toughening in the presence of deformation. Zachs and Lubahn (130) discovered that the tensile strength of cast steel specimens depended relatively little on the strength of the initial material. It is known that, under operating conditions, the strength of complex profile parts, made of cast steel with a high ultimate strength and a low plasticity, may be below the strength of similar

parts made from steel which has lower ultimate strength, but higher plasticity. Thus, the similar behavior of cast and powder metals can also be seen in this case.

In those cases, when the behavior of cast and powder metals is the same, it is, probably due to similar causes, and the study of powder metallography may be useful to the better understanding of such phenomena

91 -- The Changes in the Intergranular Contact in Compact Metals

Practically, there is a certain incompleteness of contact between the grains and a certain intercrystallite porosity, which cannot be fully eliminated by compression and annealing, even in the case of the most highly consolidated cast metals.

The porosity of compact metals is relatively low, usually tenths of a percent, but may attain a value of 1 - 2 percent, at times even higher. Tammann and Bredemeyer⁽¹⁴⁸⁾ established the following intercrystallite porosities: 2 percent in rolled zinc, 1 percent in iron, 0.6 percent in copper, 0.1 - 0.5 percent in brass, 1.1 percent in cast iron. The study of the change in porosity with annealing, in the case of compact metals, is made difficult by the low absolute values of porosity. This is the reason for Bochvar's ⁽¹⁴⁾ remark that these changes are "adequately complex to require more detailed study."

The changes in density and their effect upon the mechanical properties can be studied with greater facility in the case of

powder metals than in the case of cast metals.

The consolidation of cast metals in annealing (See paragraph 58, Table 45), as well as that of powder metals, is induced basically by the greater mobility of the metal atoms in the free surface (the surface of the pores) than near the contact sections. The mechanics of the constriction of the atoms toward the contact sections were already analyzed in Paragraph 61. In deformed cast, as well as powder metals, due to the higher mobility of the atoms in the non-contact sections of the grain surface, consolidation sets in at lower temperatures than recrystallization. Such changes in the properties of the deformed metal, after annealing, at the temperatures of regression (repose), as the increase in electrical conductivity and plasticity, are to a certain extent connected not only with the reduction in residual stresses, but also with growth of contact between the structural elements of the metal.

This "contact" shrinkage in deformed cast metals, as well as powder metals, proceeds even more intensively at annealing temperatures, which are somewhat higher than the temperature of the beginning of recrystallization. In addition, the growth of intergranular contact, in the presence of recrystallization, is also intensified as a result of the transition of intercrystallite pores into intracrystallite ones.

In addition to the "contact" shrinkage in the annealing of deformed cast metals, as pointed out by Bochvar⁽¹⁴⁾, some importance is attached to the increase in density and intergranular con-

tact as a result of the spaces between the grains being filled by thermal expansion. It should be noted that thermal contraction in cooling, on the contrary, leads to a certain non-reversible reduction in the contact between the grains.

The bond between the structural elements (grains) of cast metals is much stronger than between the particles of powder briquettes. Hence, the phenomena of the diminution of intergranular contact and the drop in density with annealing, are less pronounced in cast metals as compared to powder briquettes. Thus, the residual stresses in the annealing of compact metals, in contradistinction from powder briquettes, seemingly do not induce any reduction of contact and density. The effect of gases upon the changes in the density of powder metals is rather passive than active, and reduces itself not to a bulging-out effect due to the liberation of the gases, but rather to a certain slackening in the "contact" shrinkage (See Paragraph 79). By the same token, no disruption of contact between the grains, during the annealing of deformed sound castings of compact metals, is to be anticipated. If such an active effect of gas were present, the rate of recrystallization would frequently become diminished with the rise in temperature. Actually, a reversed ratio between the rate of grain growth and temperature is observed.

The greatest effect upon the diminution of intergranular contact, upon the drop in density and the related attenuation of

properties particularly, plasticity, which occurs during the annealing of cast metals, is due to the zonal isolation of shrinkage (See Paragraph 64, Figure 89, and Paragraph 71, Figure 109). As established in the case of powder metals, zonal isolation is progressing with the increase in the rate of shrinkage and recrystallization. Therefore, it is most sharply pronounced at high temperatures (overheating and overburning) and in the presence of great numbers of mobile atoms (i.e., with the fine granular structure and considerable size of the free surface in the initial metal). In powder metals, the baking temperatures, at which occurs reduction in contact, density, strength, plasticity, and electrical conductivity (overheating), and the fracturing of the articles (the temperature of overburning), are reduced with the increase in the free external surface (with the reduction in the thickness) of the specimens. The overburning of powder metals is preceded by buckling, the occurrence of which is accelerated by the presence of large free external surface. It being the case that the temperature of overheating and, particularly, the temperature of over-burning, are always higher than the temperature, at which the visible growth of the grain begins. Fully similar phenomena occur during the annealing of deformed cast metals. The external appearance of an overheated copper wire testifies to the presence of zonal isolation during the overheating of deformed cast metals (See Figure 151). In this case, the isolation zones coincide with the individual grains. The grain boundaries in the surface and the voids between them (particularly, where three crystallites abut) are visible even without resorting to pickling.

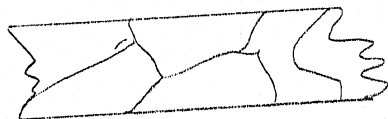


Figure 151. Overheated copper wire (according to Tammann).

The appearance of overheating and overburning in deformed cast metals is governed by the following regularities.

(1) The annealing temperatures, in the presence of which the contact between the grains, plasticity, and electrical conductivity are reduced, are always higher than the temperature of the setting-in of recrystallization (40 percent of the absolute melting point) in deformed cast metals. In most cases, they oscillate (depending on the thickness of the specimen, the degree of deformation, the size of the grain, the atmosphere of annealing, the rate of heating, the temperature time-lag, the presence of admixtures, and the like) within the range of 60 -- almost to 100 percent of the absolute melting temperature of the metal. Thus, in the experiments conducted by Sachs, the drop in plasticity (elongation) of aluminum was recorded only after annealing at temperatures above 300 degrees Centigrade (about 60 percent of the melting point), and in the experiments by Chokhralskiy -- only at temperatures above 600 degrees Centigrade (i.e., more than 93 percent of the melting point) (14).

(2) The temperatures of the clear drop in plasticity and

electrical conductivity are reduced visibly with the diminution of the free surface (reduction in thickness) of the specimens. Thus, by the data of the Manual of the US Bureau of Standards, no essential reduction in the plasticity (reduction in area and elongation) of 22- millimeter nickel rods, annealed at 1100 degrees Centigrade (about 80 percent of the melting point), is visible. However, in the annealing of fine nickel wire (0.375 millimeters), a sharp drop in elongation occurs at temperatures above 700 degrees Centigrade (57 percent of melting point) and in the case of still finer wire (0.04 millimeters) -- the drop in elongation occurs at temperatures above 650 degrees Centigrade (53 percent of melting point). Tammann⁽⁶⁰⁾ cites some data on the drop in electrical conductivity after the annealing of fine (0.2 - 0.5 millimeter) gold, silver, copper, and nickel wires. The maximum value of electrical conductivity occurred at the point of 63 - 80 percent of the absolute melting point. It should be remembered that in such fine wires, the magnitude of the external surface and that of the contact surface of the grains is approximately the same.

(3) Overburning is promoted by annealing in an oxidizing atmosphere.

These regularities mentioned above are the same as those present during the annealing of powder metals.

The reduction in the size of the grain, which is sometimes observed with the rise in the annealing temperature (See Paragraph 71, Figure 104) can also be explained by the presence of zonal isolation. Such a decrease in the size of the grain, with the

rise in the annealing temperature, was observed by Bochvar, Belov, and Gramovskiy (21).

92 -- Admixtures in Cast Metals.

Admixtures, entering into solid solutions and intermetallic compounds with the basic metal, increase the strength, reduce the plasticity (in a number of cases), and practically always, greatly reduce the rate of all the processes, linked to the mobility of the atoms. Stanley (145) observed that, with the increase of the silicon content in iron from 1 to 3.1 percent, the rate of the grain growth diminished 4 - 5 times. According to Austin, Jones, and Lindsay, the rate of creep ($\sigma = 3.5$ kg/sq mm, $t = 540$ degrees Centigrade), when adding 0.59 percent silicon to the iron, was diminished 140 times, when adding 0.11 percent molybdenum -- 180 times, when adding 0.45 percent chromium -- 10,000 times.

Intercrystallite admixtures are also of great importance in cast metals. The indisputable contribution made by Tammann is his empirical proof of the existence of continuous films of admixtures ("intercellular substance") in cast metals. These continuous films attenuate the mechanical properties and hinder the recrystallization in the case of non-deformed cast metals. There is adequate empirical data, confirming this thesis by Tammann not only in the case of cast metals, but also in the case of powder metals. One of the principal causes of the rise in the temperature of the beginning of recrystallization in powder metals (66 - 75 percent of the melting point), as compared to deformed

cast metal (40 percent of melting point), is the presence of the continuous oxide films in the powder particles (See Paragraph 68). Only after the reduction of a considerable part of the oxides at temperatures of about 66 - 75 percent of the melting point, the growth of the grain begins. In powder metals with difficultly-reducible oxides (as, for instance, aluminum) the growth of the grain does not occur even at temperatures close to the melting point. The presence of a considerable amount of oxides causes the diffusion of carbon and the formation of iron carbide in the metal-ceramic alloys of iron to occur at higher temperatures (about 75 percent of melting point) than during the cementation of cast steel (See Paragraph 83). There are even numerous examples of the detrimental effect of the non-reducible oxides upon the mechanical properties of baked powder metals.

The continuous films of intercrystallite admixtures are formed during the crystallization of smelted metals. They may be formed as a result of the precipitation of the admixtures from the solid solution at the boundaries of the grains during the cooling that follows the annealing of the metal. According to the opinion of Tammann himself, these continuous films are formed not only during the cooling, but also during the annealing of the deformed metal. Tammann assumes that, in recrystallization, the inter-crystallite admixtures, in redistributing themselves in the diminishing surface of the grains, isolate a part of the surface, which becomes reduced with the growth of the grain, and finally, form the continuous films. This process, according to Tammann, is the specific cause for the retardation and the cessation of the growth of the grain, with the time-lag of annealing.

Powder metallography furnishes adequate theoretical and empirical proof that the formation of the continuous films during the process of annealing (but not during the process of cooling) is not much probable. Let us analyze the case, when the intercrystallite substance is capable of dissolving a small amount of the basic metal, and that it is liquified in annealing (See Figure 152, a). In this case, the basic metal will be dissolved more rapidly further away from the places of intergranular contact, and will be precipitated more rapidly from the solution near the places of contact. As a result, the isolation of the contact surface by the admixtures becomes diminished (Figure 152 b). If the intercrystallite admixtures are not liquified in annealing, only the rate of this process, but not its direction will change (See Paragraph 84). The experiments by Dawihl and Hinnlbor pertaining to the dissolution in the tungsten carbide - cobalt alloy of the cementation phase (cobalt), which, in this case, can be considered to be the intercrystallite phase, were related in Paragraph 84. These experiments revealed that, during the baking, the direct contact between the grains of the tungsten carbide is continuously being increased. The intercrystallite admixtures can undoubtedly retard the initial rate of grain growth, but they can hardly cause retardation and cessation of grain growth, with the increase in the duration of recrystallization.

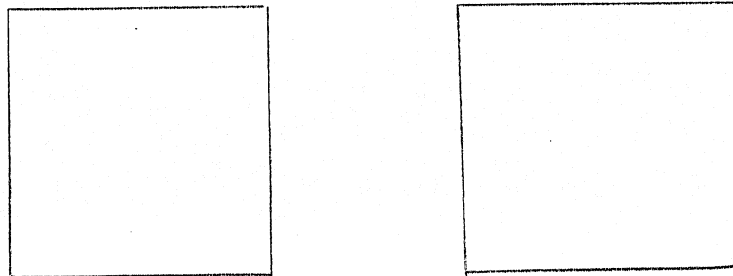


Figure 152. Intercrystallite admixtures:

a - prior to annealing; b- after the annealing of the metal -- the admixtures are cross-hatched, the grains are not (the representation is merely diagrammatic).

The modern technique of powder metallurgy is based on the ever widening use of admixtures, which, in forming a second "intercrystallite" phase during the baking process, running for a more or less protracted period, promote the growth of the grain and increase the contact between the grains. Thus, in order to obtain monocrystal tungsten wire, oxygen and halogen compounds of metals are added (See Paragraph 67). In order to increase the contact between the particles in metalloceramic alloys of iron and copper, the addition of small quantities of phosphorus, less frequently sulfur, is resorted to ⁽¹¹¹⁾. Such additions, in forming with the basic metal, during some part of the baking period, easily-fusible entectoids, promote the improvement of intergranular contact. The study of these effects exerted by admixtures is of unquestionable interest to metallography in general.

93 - Powder Metallography and the Crystallization of Fused Metals

Powder metallography embraces, amongst other problems, the baking of two-phase solid-liquid systems, in which the solid component forms the continuous skeleton, while the liquid component is usually present in the amount of 5 - 30 percent - volumetrically (See Paragraph 84). If pores are present in such powder alloys, there is intensive "contact" shrinkage of the solid skeleton during the baking process. In principle, the mechanics of this "contact" shrinkage are the same as in the shrinkage of a single-phase powder metal. The liquid phase, as well as the pores, do not hinder the translocation of the solid skeleton. Hence, the contact shrinkage of the skeleton can continue also with the complete closing of the pores. Its result, in this case, will be not a diminution of porosity, but liquation -- the translocation of the solid phase toward the center, and the liquid phase --- toward the periphery of the specimen. For instance, in the baking of powder copper-lead alloys, the liquation of lead into the external zones is increased with the diminution of the porosity in the initial briquettes. In connection with the phenomena of liquation, the contact shrinkage of the skeleton may result, regardless of how paradoxical it may sound at first, in an increase, and not a reduction of porosity. This explains, to a certain extent, the fact that, with high porosity of the initial briquettes, the shrinkage in powder copper-lead alloys is considerably greater, and with low porosity of the initial briquettes, it is, on the contrary, con-

siderably less, than in the case of pure copper powder (See Figure 136).

It is not only powder metallurgy that is called upon to deal with two-phase solid-liquid systems. During the solidification of cast alloys, after the formation of the continuous skeleton, we are dealing with a similar solid-liquid phase. The shrinkage of the solid skeleton in cooling, the so-called linear shrinkage, was investigated in detail by Kochvar and his collaborators⁽¹⁷⁾. According to him, the linear shrinkage, specifically, is the principal cause of shrinkage stresses and fissures, which reduce the properties of the cast metal. He ascribes the linear shrinkage to thermal contraction in cooling. It can equal the product of the mean coefficient of expansion by the difference between the temperature of solidification and room temperature, or due to the interval of crystallization, its value may be less than the above product. Korol'kov⁽³³⁾ discovered recently that, in pure metals, the linear shrinkage is determined precisely by thermal contraction. However, Dobatkin⁽²⁸⁾, in turn, proved that in the very rapid cooling of castings, the linear shrinkage of duralumin attains the value of 2.4 to 2.5 percent, i.e., almost $1\frac{1}{2}$ times greater than its thermal contraction. The author considers that this result, in addition to the causes referred to by Dobatkin, may also be due to the contact shrinkage of the skeleton. Since the liquid phase can be translocated in a direction normal to the linear shrinkage, the contact shrinkage may lead not only to liquation, but also to an increase in linear shrinkage beyond the extent

stipulated by thermal contraction. The prerequisite for considerable contact shrinkage is precisely the very rapid cooling of the casting. In slow cooling, the formation of the skeleton and the final solidification of the casting are not simultaneous in the various places of the casting. Hence, the inevitable zonal isolation of contact shrinkage, which can attenuate it considerably or even reduce it to zero. During the slow cooling of the metal, a continuous incrustation is first of all formed at the walls of the mold, which incrustation hinders the subsequent contact shrinkage. (See Figure 94). When cooling is accelerated, the formation of the skeleton and shrinkage occur more simultaneously, as a result of which the effect of zonal isolation is diminished. Hence, with an increased rate of cooling, shrinkage must increase. According to Dobatkin, with the rate of casting equal to 4.2 meters per hour, the linear shrinkage of duralumin was 1.97 percent, with the rate of casting equal to 9.0 meters per hour -- 2.36 percent, and with the rate of casting equal to 11.5 meters per hour -- 2.40 percent.

The "contact" shrinkage of the hard skeleton is, in the opinion of the author, one of the principal causes for the inverted liquation in alloys. Two processes take place during the solidification of a smelted mass: the equalization of the composition of the liquid phase, as a result of diffusion and convection currents, and the "contact" shrinkage of the solid skeleton. In the solidification of the casting, the external layer, richer in the refractory component, becomes crystallized first of all. Diffusion and convection, conveying into the liquid at the crystal

boundaries new quantities of the refractory component to replace the quantities already crystallized, promote normal liquation -- the enrichment of the external layer with the refractory component.

The "contact" shrinkage, in constricting the solid skeleton toward the center, is conducive to inverted liquation -- the enrichment of the external layer with the easily-fusible component.

Bauer and Arndt (79) pointed to the connection between inverted liquation and the formation of dendritic crystals. Since the latter have the greatest surface, the shrinkage constriction, in this case, will be of a maximum value. In addition, the shrinkage, leading to inverted liquation, will only begin at the moment of the formation of the continuous solid skeleton, which, in the case of dendritic crystallization, is formed earlier.

Figure 153 is a curve graph depicting the inverted liquation in the alloys of tin and zinc, according to Dzhokibe. In the presence of a too small concentration of the more refractory component, which is precipitated first of all, the inverted liquation value equals zero, since the constriction pertains only to the crystals in contact with each other, but not to the isolated crystals. Inverted liquation begins only after a certain minimum concentration of the more refractory zinc (beginning with 15 percent) has been effected, and increases gradually until an approximate 50 percent concentration of zinc. With a concentration of refractory component in excess of the above, the inverted liquation will diminish again as a result of the phenomenon known in powder

metallography as the reduction in the constriction of the crystals with the increase in the density of the packing (See Paragraph 75).

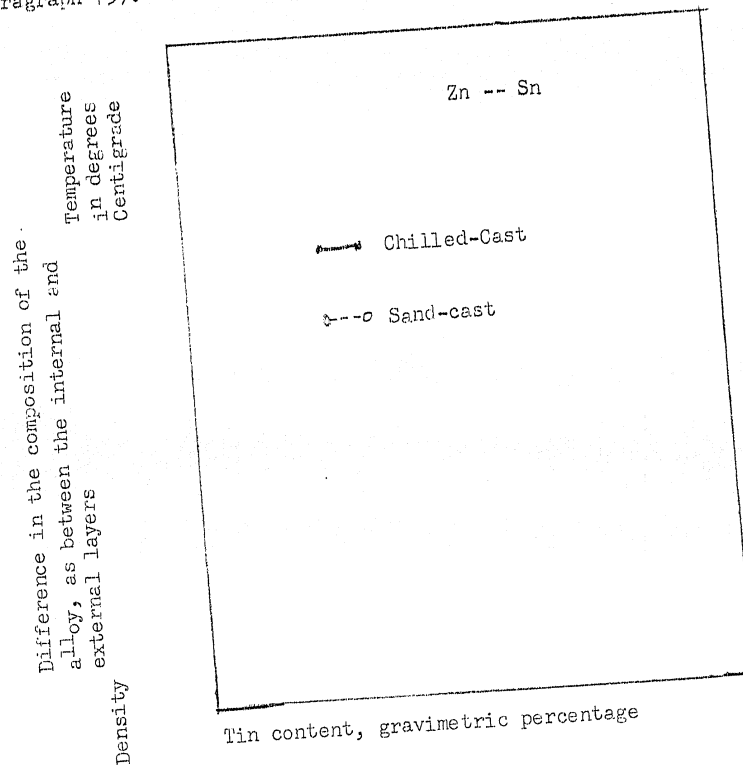


Figure 153. Inverse liquation of tin & zinc alloys (Dzokibe).

The experiments of Boner pertaining to the effect of the rate of cooling upon the liquation of aluminum with 4 percent copper content. With low rates of cooling, diffusion comes through, besides, the specific surface of the precipitated crystallites is small, hence a normal liquation takes place. With high rates of

cooling, the normal liquation is changed to a strongly pronounced inverted liquation, since the time was too short for the equalization of the fused mass to take effect. With still higher rates of cooling, the inverted liquation is again diminished, since a certain period of time is required for the contact shrinkage of the skeleton to take effect.

The methods of powder metallography may be useful in the solution of the most variegated problems linked to contact phenomena -- the study of phase transformations, graphitization of cast iron, processes of diffusion, and the like. The more familiar the wide circles of metallurgists become with this branch of science, the greater will be its effect upon the progress of metallography in general.

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